TEXT-BOOKS OF SCIENCE

ADAPTED FOR THE USE OF

ARTISANS AND STUDENTS IN PUBLIC AND SCIENCE SCHOOLS

PHOTOGRAPHY

A TREATISE ON

PHOTOGRAPHY

BY

SIR WILLIAM DE WIVELESLIE ABNEY, K.C.B.

D.C.L., F.R.S.

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PREFACE

TO

THE TENTH EDITION

THE publishers having called for another edition of this work, it became necessary to take into account the different degrees of importance that the present processes in Photography hold, and to render more prominent those which have proved to be the most generally employed. This entailed recasting of the work in a great measure and making numerous and somewhat large additions to its pages in order to bring it up to date. It will be found that photo-block printing processes have been described, and that orthochromatic and three-colour processes of photography have been explained, together with other printing processes which are now extant. Notice of new researches on the theoretical side of photography are also included, and will be found of some interest to the scientific photographer for whom these pages have been mainly written. The numerous editions through which this work has passed lead

the author to hope that this latest one will be equally successful, and that it will be found to contain all the latest information as regards the science and practice of this fascinating art. It cannot, however, pretend to be a manual suitable for specialists in any particular branch of photography, but it is believed that it contains sufficient information and directions to enable the amateur to experiment with the various processes with success.

October 1901.

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A TREATISE

PHOTOGRAPHY

CHAPTER I

HISTORICAL SKETCH OF THE DISCOVERY AND PROGRESS OF PHOTOGRAPHY

To the alchemists of the sixteenth century belongs the honour of having first noticed the change that took place in silver chloride (known to them as 'Luna cornua') by exposure to light, but they regarded the darkening as a species of transmutation of metals, and it remained for Scheele, the Swedish chemist, in 1777, to investigate the properties of this compound, though his researches led at the time to no practical end. Scheele found, when he exposed silver chloride to the action of light beneath water, that in the fluid was dissolved a substance which, on the application of silver nitrate, gave once more silver chloride, and that, after applying ammonia to the blackened body, an insoluble residue of metallic silver remained behind. These were the only facts elicited at the time, and a delay of more than half a century occurred before they were put to really good purpose. In 1801 Ritter, of Jena, repeated the experiments of Scheele, and discovered that the chloride darkened rapidly in those rays of the spectrum which lie beyond the extreme violet. To him also is due the announcement that the red

rays have the property of undoing the work effected by the violet, though he attributed the effect to the wrong cause.

In 1802 Thomas Wedgwood read a paper before the Royal Institution, entitled 'An Account of a Method of Copying Paintings on Glass [1] and of making Profiles by the Agency of Light upon Nitrate of Silver.'

With these experiments of Wedgwood's Sir Humphry Davy was associated, and in their record we find it stated that muriate of silver was more readily acted upon by light than the nitrate, and that white leather used as a basis gave better images than paper. Images obtained by the solar microscope were impressed without any serious difficulty, but no means was discovered of rendering them anything but transitory when exposed to daylight. For Charles, a Frenchman, has been claimed the credit of employing at an earlier date the same method of obtaining black profiles by the action of light, but there seems to be no authentic proof extant that this claim should be allowed. Dr. Wollaston, in 1803, discovered that gum guaiacum, when exposed to the action of the blue rays of light, became changed in colour, and that on exposing those altered portions to the red rays, the original tint was restored.

In 1814 Photography was to receive a new votary in the person of Joseph Nicéphore de Niépce. Leaving the salts of silver, he devoted himself to the study of the action of light on resins. After several years of research, he at length completed the process known as heliography, which consisted in the production of a picture in bitumen on a polished metal plate. The discovery he made in regard to this resin was that, after insolation, it became insoluble in its ordinary solvents. An exposure of many hours in a camera obscura was necessary to produce the required effect; hence, as may be imagined, the views taken by this means

[1] A mistake often occurs in the reading of this sentence. Wedgwood did not make the copies on glass, but copied paintings which were drawn on glass.

were wanting in vigour, owing to the shifting direction of the sunlight, and, as we shall see later on in this work, from other causes, were of necessity deficient in delicate lights and shades. In 1827 Niépce came over to England, with the intention of drawing the attention of the Royal Society to his discovery, but, his process being secret, his communication was not received, and he returned to France. In 1824 Daguerre, a French painter, began a series of experiments in the same direction, and in 1829 he and Niépce entered into a partnership, and presumably it was the knowledge of the latter's method of working which gave the former the idea of the daguerreotype. Niépce had employed silver plates covered with asphaltum, which, after exposure and application of the solvent, left the metal bare in parts. The image thus formed was brown; the shadows being represented by the metallic surface. In order to produce a proper effect, it was necessary that the parts covered by the bitumen should be whitened and the bare parts darkened. After various experiments, he applied iodine to the picture, subsequently removing the bitumen. It is to be presumed that Daguerre noticed the action that the light produced on those portions of the plate which had been converted into iodide. At any rate, to Daguerre belongs the glory of the discovery that an image could be produced on a silvered plate which had been exposed to the vapour of iodine, though it was by fortuitous circumstances that he hit on the method of developing an invisible image.

In January 1839 the discovery of the daguerreotype process was first announced, and in August of the same year the details of production were given to the world, Daguerre and Niépce the younger (the successor of Nicéphore) obtaining a pension from the Government of France. Whilst Daguerre was working in France, we find that one of our own countrymen, Fox Talbot, had been experimenting in another direction. Bearing in mind the work of Scheele and Wedgwood, he devoted himself to the production of

drawings &c. on silver chloride, and in January 1839 he read a paper before the Royal Society on 'Photogenic Drawings.' His method of procedure was somewhat as follows: Writing paper was coated with a solution of common salt, and after drying was brushed over with silver nitrate; by this means silver chloride was obtained, with a slight excess of the nitrate, in which condition it proved excessively sensitive to light. Various bodies, such as lace and ferns, were laid on this paper, and a reversed facsimile of them in black and white was produced, and he fixed the

FIG. 1.

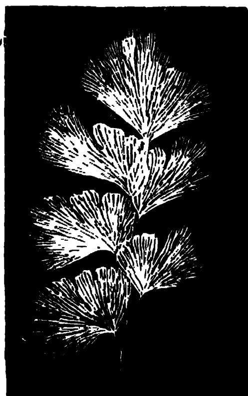


FIG. 2.



impressions by solutions of bromides and chlorides. When such a reversed facsimile was placed over similarly prepared paper, and the light allowed to act through it, the result was the formation of a facsimile, only this time not reversed in shades.

These two prints were respectively named the negative and the positive (fig. 1 and fig. 2).

Comparing this process with the former, we see what an immense advantage Talbot's process had over the daguerreotype. With Talbot's any number of copies of a subject could be cheaply produced, whilst with the latter

one positive was the sole result, unless expensive electro-chemical means were resorted to.

The Rev. J. B. Reade was also an ardent experimentalist in this process, and to him is to be ascribed the discovery of the accelerating power of gallic acid, in the presence of silver nitrate, for the production of an image, and also for the *development* of the invisible image by the same agency.

From this discovery, together with that of Daguerre's, Fox Talbot reasoned out the calotype process, which he patented in 1841. By it an invisible image is formed on silver iodide on paper, and developed by gallic acid. In this process of Talbot's a negative image was formed, while by the first process the positive pictures were produced; and it should be remarked that the same method of producing silver prints obtains to the present day with scarcely any alteration.

Sir John Herschel had drawn attention to the possibility of producing photographic pictures on glass, and in 1843 had actually printed, in a camera obscura on silver chloride, deposited on such a plate, a picture of his 40-foot telescope. Niépce de St. Victor made a further great advance when he succeeded in holding the sensitive salts of silver on glass by using albumen as a vehicle, but to Le Gray must be accorded the credit of suggesting collodion as suitable for retaining them *in situ*. Scott Archer, with whom was associated Dr. Hugh Diamond, in 1851, however, introduced the collodion process in the practical form in which it exists to-day, and it may safely be said that, with the exception of the daguerreotype process, no more important discovery in photography has been made.

In 1839 Mungo Ponton published the fact that potassium dichromate, when applied to paper and dried, altered in composition when exposed to the influence of light. This announcement caused much investigation into the subject, and it was subsequently discovered that not only was the chromate altered in composition, but that the sizing

of the paper was oxidised. Gelatine, gum, starch, albumen, were all found to become insoluble when exposed in contact with it; and Poitevin utilised this fact in the production of pictures in powdered carbon by a process analogous to that subsequently to be described in these pages. Swan, Johnson, Woodbury, and others, have more recently extended its application by the production of images formed in gelatine, coloured with pigments; whilst a still wider field has been opened by Albert, Edwardes, and others, in the production by mechanical means of prints in printers' ink from a gelatine image, founded on the fact that oxidised gelatine is incapable of absorbing water.

CHAPTER II

EXPERIMENTS WITH LIGHT

BEFORE entering into the theory of photography, it will be convenient to enter briefly into some of the phenomena of light; for it is with this form of energy that the photographer has to deal. It will be as well first to try one practical experiment with light, in order to clear up certain difficulties which may present themselves.

Darken a room of some 12 or 14 feet in length by means of shutters (light wooden frames covered with opaque paper will answer), and in one fix a small plate of glass, A, which has previously been covered with tinfoil, and on which, with a sharp knife, has been cut a straight line laying bare the glass; on a table place a glass prism, B, the centre of which is at the same height as that of the slit, and have a screen, covered with white paper, C, and a lens, E, of about 12 inches' focus, ready at hand; outside the window arrange a mirror, D —an ordinary looking-glass will answer—in such a position as to reflect the sunlight on to the slit: interpose the lens, E,

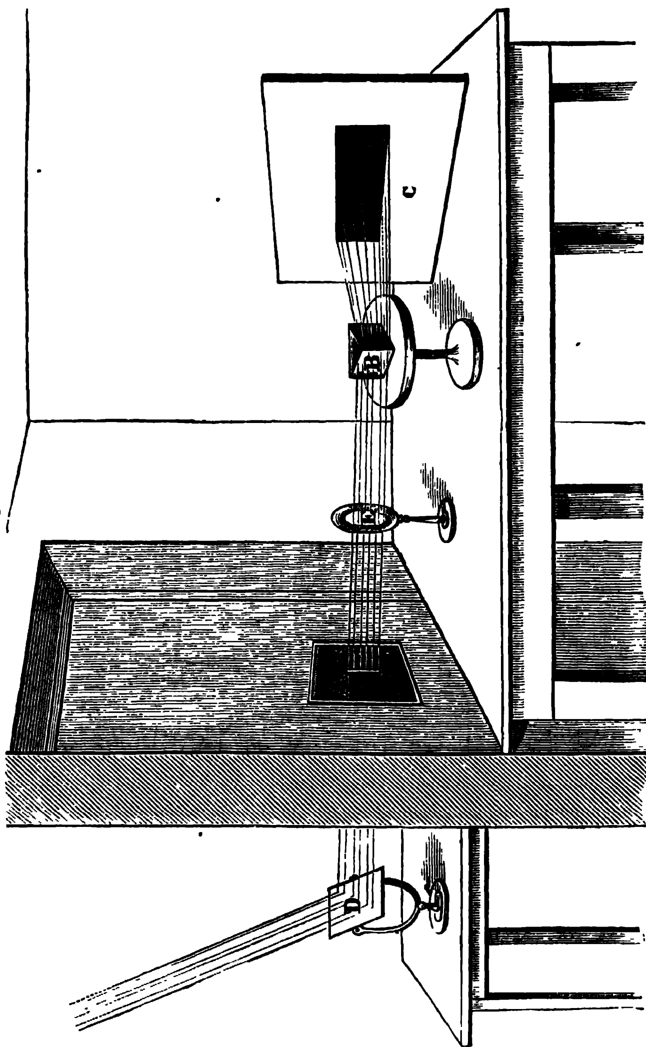


Fig. 3.

about 6 inches from A, in such a manner as to cause the beam to fall upon the prism, B. The floating dust in the room will immediately show that the original beam of white light has been split up into a series of coloured rays, and a position for the screen may then be found which will cause the top and bottom edge of the spectrum (as this glorious band of colour is termed) to be sharply defined; and if the cut in the tinfoil be fine enough, a series of dark lines will traverse it vertically. With these, however, we have nothing to do at present. Now experiments, the results of which have formed the groundwork of mathematical reasoning on the theory of light, have conclusively proved that light *as* light is merely a sensation. Permeating all known space is assumed to be an imponderable and elastic fluid known as ether, and in it a luminous or heat source is able to generate a series of ripples or waves, flowing unbrokenly and continuously from it. What the prime form of these undulations may be we cannot tell. They may be, and most probably are, compounded of an almost infinite number of different undulations, when ordinary [1] white light is the impression given to the eye, and each of these series of undulations varies in length from crest to crest. Those of certain lengths are able to affect the nerves which line the retina of the eye; whilst some of these are able to affect other nerves lying in our bodies, producing the sensation of heat; others again, though incapable of producing the sensation of light or heat, exhibit themselves by their effect on certain compounds, causing chemical combination or decomposition. Of those waves whose impact on the eye produces the sensation of light the shortest is about 600 millionths of a millimetre, whilst the longest is about 350 millionths of a millimetre. The former give the sensation of a violet colour, the latter of a brilliant red. Examining the spectrum thrown on the screen, the intermediate colours of blue, green, yellow, and orange are seen, and the wave-lengths producing their effects

[1] *i.e.* not polarised.

on the eye lie intermediate between the limits given above. There is uncertainty as to the lower limit to which the heat-producing rays are refracted, but probably to a length equal to that of the visible spectrum, whilst the range in length of the chemically active waves other than those situated in the visible portion of the spectrum, and which lie beyond the violet (being called the ultra-violet or fluorescent rays), is, if anything, still more uncertain. It will be evident on reflection that it must be accidental that, between certain limits, the waves should be capable of producing a sensation of light or of heat. The exact upper limit of the thermal spectrum is unknown, but from theory it must be coterminous with the chemically active rays; as will be seen further on, the inferior limit of the capacity of any waves to produce decomposition is as yet unascertained. All those series of waves which effect decomposition in any compound are called *actinic* rays, and, as will be seen, the range of these varies for every ordinary photographic compound.

It may help us in a right comprehension of our subject if reference is made here to one quality of these undulations. The interstellar ether in which these waves ripple is assumed to permeate every body, solid, liquid, and gaseous; and it depends upon the disposition of the ultimate molecules of the body whether it is opaque or transparent to any of the visible or dark rays of light. It must be borne in mind that the molecules of every substance are presumably in a state of vibration, the extent and velocity of which depend partly upon the temperature, and partly upon the nature, of the substance, and that this must ever be so unless the purely theoretical condition of absolute cold be arrived at. Supposing, then, we have a glass, which with white light falling on it allows only the transmission of red light, and we look through it at the spectrum formed by white light, we should find that it cuts off the whole of the colours excepting the red, obliterating them more or less perfectly; that is, in technical language, it absorbs them. Now, according to all

ideas of the conservation of energy, this absorption must indicate the performance of some kind of work. It may be that it causes the already vibrating molecules of the glass to take up and swing in some complicated manner with those rays particularly absorbed, and thus to cause a rise in temperature in the body, so small indeed, perhaps, as to be indistinguishable, owing to the rapid cooling due to radiation; or it may be that work is performed in effecting chemical decomposition, for even glass is thus affected by light. The rays which simply pass through the glass produce no effect on it—their energy is unimpaired.

It should also be noted that where light is not entirely absorbed, but is only reduced in intensity, even then also work must be performed by it; for the intensity of any coloured or white light is dependent on the extent, or amplitude, as it is termed, of the wave or waves; and any diminution of the amplitude indicates that a portion of its available energy has been exhausted, and that therefore a transference of the portion so expended must have been made to the body through which it passed. This exchange or transference of energy is an important subject in all photographic matters; it explains many of the phenomena in photography which often present a great difficulty to the beginner or to the rule-of-thumb photographer, whilst it is all-important in the right understanding of the revelations which are made by the spectroscope.

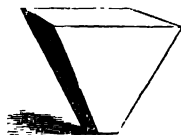
It may then be laid down as an unalterable law, that *where there is absorption of light (whether of dark or visible rays) by any body, work of some description must have been performed in that body.* An account of the valuable experimental research of Joule on the mechanical values of light and heat is given in the 'Philosophical Magazine' for 1843, and is deserving of special study.

CHAPTER III

THEORY OF SENSITIVE COMPOUNDS

EVERY particle of matter may be considered to be made up of molecules, each molecule consisting of constituent atoms. Thus a particle (and when we say particle we mean to convey the idea of the smallest visible quantity of matter) of silver iodide is composed of molecules of a like definite composition, the components being—two atoms of iodine and two of silver, or multiples of these numbers. The physical aspect of matter often conveys to the mind an idea of a certain kind of arrangement in the molecules; as does the analysis of a compound, if not of the absolute arrangement of the atoms, at all events of the arrangements which they cannot take. Oxalic acid, for instance, we know is composed of carbon, hydrogen, and oxygen, having the formula $C_2H_2O_4$, or the exact equivalents of water (H_2O), carbon monoxide (CO), and carbon dioxide (CO_2), yet the compound is totally different in its physical characters and chemical reactions from any of these. From this we can argue that the atoms of its molecules must be separated in such a manner that the oxygen molecules cannot seize upon the hydrogen to form water, or on carbon to form carbon monoxide or dioxide. When the atoms are so arranged as to be incapable of forming a molecule of a simpler type, they occupy a position of excessively stable equilibrium, and it would be necessary to expend a large amount of work to separate them. On the other hand, where the atoms of the molecule are so grouped that by rearrangement they may form perhaps more than one molecule, each of which may be

FIG. 4.



of less complex character, it often happens that all the atoms are in a state of stable, though verging on indifferent, equilibrium. We may take as an illustration of this state of equilibrium the frustum of a pyramid standing base uppermost, on a narrow section parallel to the base. It is apparent that the work expended in order to cause the frustum to find a new position of more stable equilibrium (or, in other words, to fall on to one of its sides) may be made as small as we please by diminishing the area of the section on which it stands. Whilst falling, the body can do a certain amount of work, which will be quite independent of the amount of work expended to cause its fall. So with the atoms of a molecule which are in this state of almost indifferent equilibrium ; a very small amount of work need be expended in order to cause them to take up more stable positions ; but the kinetic energy they may possess whilst passing to this new state need be no measure of the work performed upon them. A measurement of the work performed by their rearrangement would principally tell what amount of work had been expended in some chemical process, in order to place them in that state bordering on indifferent equilibrium. It is *possible*, however, under certain circumstances, to compare two or more energies with one another, by comparing the effects they produce on such molecules. Extending our previous illustration, supposing we had a row of such frusta of pyramids, and that it was found that one pellet of a number (all being of equal weight) when striking one frustum with a certain velocity, was able to cause it to fall, and also that in every case the accuracy of aim was undoubted, and that in falling one frustum did not strike its neighbour; then at any interval after the commencement of a bombardment the amount of work expended in projecting the pellets could be compared by simply counting the number of frusta which had fallen.

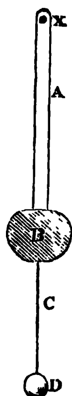
It is in a manner akin to this that the comparative values of the intensity of those rays which produce chemical

decomposition in sensitive compounds are found. The molecules of the compound answer to the frusta, and the pellets to the number or amplitude of the waves impinging on them. The method of estimating the number of molecules altered in composition is by noting the colour or the attractive power on other matter which they possess. In our illustration we assumed that one frustum never interfered with another during its fall, and, so far as the compounds, which are photographically sensitive, are concerned, this is a correct assumption, for the alteration in one molecule does not cause an alteration in the neighbouring one. In other sensitive compounds this may not be the case. It is frequently the case that the rearrangement of the atoms of a molecule calls into play such a large amount of kinetic energy (it may be in the form of heat), that the neighbouring atoms are caused to rearrange themselves, and so on. In this case the destruction of the original form of the molecules may be so rapid, and the potential energy converted into kinetic may be so large, that we may have a compound which is an explosive. With these latter compounds the energy existing in a vibration is often sufficient to cause explosion. The vibration may be that of the longer waves produced in the medium we have already discussed, or may be those produced in the atmospheric or other gases. Thus, radiant heat may cause it, as also sound. It has been experimentally proved that many explosives are particularly sensitive to vibrations of a definite wave-length; thus, the vibration to which nitroglycerine is most sensitive is not the best with which to cause the explosion of gun-cotton. It has also been asserted that the atoms of the molecules of iodide of nitrogen can be caused to be dissociated by the atmospheric waves which are due to sound of a particular pitch.

In order to understand more readily how it is that the molecules of such bodies may be disturbed by waves of a certain length, it must be recollected that they are in a state of agitation. In solids the paths they describe are limited,

though the excursions they take will be the greater the higher the temperature of the body; and from analogy it may be assumed that the agitation is really a definite oscillation, though the paths described may be very complex. Now, ordinary white light, as has already been pointed out in the last chapter, most probably consists of an almost infinite series of undulations of varying length, traversing a medium, and it is quite conceivable that the molecules of a body, whose oscillations synchronise with one of these series of ethereal waves, may have their paths altered in form, and their amplitude increased to such a degree, that a rearrangement of the atoms must ensue. In order to illustrate the effect of one oscillation upon another, the late Professor Rankine employed the following contrivance. A is a lath to which is suspended a leaden bob, B, some six or seven pounds in weight; C is a string attached to B, by which is suspended a wooden bob, D. The whole is caused to oscillate on an axis placed at X. When the length of the string is such as to cause the heavy and the light pendulum to synchronise accurately, a slight horizontal displacement of B will cause the length of amplitude of the oscillations of D to increase to such an extent that the latter will pass the semicircle and tumble. When the synchronism is only nearly perfect, the amplitude of D will at first increase, gradually stopping the oscillation of B, when it will diminish, and finally come to rest and bring B into oscillation once more, and so on. If we take the swing D as the type of the oscillation molecule, and that of B as the oscillation of the ethereal medium, it will be seen how perfect and nearly perfect synchronism will increase the oscillation of the molecule. The same illustration applies to a part of the theory of explosives, whether caused to

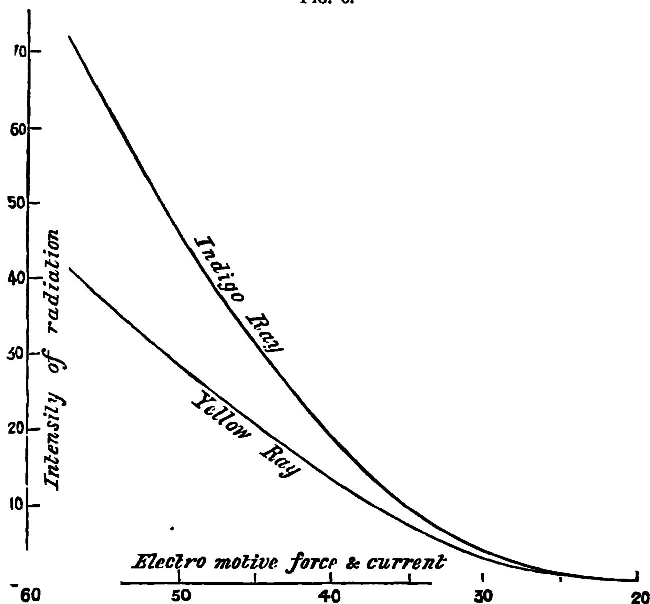
Fig. 5.



explode by the energy of radiation, or by that of atmospheric or gaseous waves. This is in accordance with what we have already advanced: it is only those waves which are entirely or partially absorbed, and whose amplitude is consequently annihilated or reduced, which can do work on a body: therefore, in choosing any particular ray of light with which to cause this class of decomposition in a compound, it is a *sine quâ non* that it must be absorbed; in addition to which, some atoms must be less loosely bound to the molecules than are others. It is found practically that the bodies employed for photographic purposes are affected principally by the waves of short length, and that as a rule those of greater length are inoperative; and here we come to a great distinction existing between the rearrangement of the atoms of the molecules, in explosives and in photographic compounds. The short wave-lengths do not affect the former, though the longer ones, which we call radiant heat, can do so. Now the *energy* transmitted from a hot and luminous body by the medium lies principally in those waves which are capable of producing what we call heat (in fact, the energy can only properly be estimated by ascertaining the heating effect due to the radiations), and as the heat produced in a body by the waves of lengths such as 450 millionths of a millimetre is insignificant, and when they are of a length of 200 millionths of a millimetre is at present immeasurable, it is evident that the energy expended on the production of these last wave-lengths is small; at the same time it happens that their production, *as a rule*, necessitates the existence of those of greater length. Thus, a platinum wire inserted in an electrical circuit may be heated, and yet only radiate dark rays; by increasing the current it may become cherry-coloured, and a spectroscopic examination will demonstrate that only red rays are emitted, whilst at the same time it may be shown that the intensity of the dark rays is increased. By further increasing the current, the

yellow, green, blue, violet, and ultra-violet rays may in succession be caused to radiate from the wire; all the first emitted rays increasing in intensity. Fig. 6 shows the relatively greater increase in an indigo ray, compared with a yellow ray, emitted from a carbon filament heated *in vacuo* by an electric current.

FIG. 6.



In order, therefore, to displace the molecules of small stability of the photographic compound which are in equilibrium, it is as a rule necessary to produce waves of great length as well as waves of short length, and this may mean the existence of a great heat energy at the primary source of radiation, though not necessarily at a reflecting surface. Now, the usual result of the displacement of an atom from what we may call the *sensitive molecule* is to form a fresh

solid body, and consequently the potential energy of the molecule is small, also the number of these molecules acted upon in a given time is small in comparison with the total; hence the kinetic energy (which may take the form of heat) that may be generated by the chemical decomposition and recombination falls far short of that required to produce even red light, much less waves of still shorter length. We thus see that although one molecule of an explosive *per se*, after its potential energy has become kinetic, can cause vibrations of such a character as to effect a disruption of the neighbouring molecules, yet a similar disturbance produced in a molecule of a photographic compound is not capable of causing an extension of the action beyond the molecule itself, and that it requires a renewed action of the disturbing force to do it. At first sight this seems unfortunate, but when we consider what would happen were such an event possible, it is apparent that the production of a photographic image in such a case would be impossible.

In a succeeding chapter it will be found that a molecule of chloride of silver responds principally to the swing of the ultra-violet waves in the spectrum, and that it undergoes a change, owing to the throwing off of one of its constituent atoms; yet the same body may, by the aid of an artifice, be fused by the dark rays of heat, which are comparatively of great wave-length, and though it in itself becomes luminous, emitting the very same rays that, when falling on it, can cause one of its atoms to be shaken off, yet it remains unaltered. In this last case the vibrations of the molecules are not of the definite character needed to cause the change. A small force, applied at definite intervals, may cause a body to attain a great amplitude of vibration. A boy may cause a violent oscillation of a church bell if he time his pulls at the rope properly, and the accumulated energy may be such that it may drag the ringer up, though the work he may have executed at each pull of the rope may be very small. On the other hand, the ringer

may expend the same amount of energy at the wrong time, and the effect on the bell will be insignificant. The experiment given at p. 14, fig. 5, illustrates this effect.

As before stated, the number of molecules affected in a short interval of time by light may be so small that their change in atomic composition may be invisible to the eye, or in *physical appearance* may be of a similar nature to the compound from which they are derived, in which case even a prolonged exposure to the actinic rays would produce no visible effect. When the sensitive compound is formed in a thin layer held *in situ* on some substratum, such as paper, glass, &c., the light reflected and radiating from an object after passing through a lens may be caused to fall upon its surface and form an image. When the rays are of such a nature as to cause the equilibrium of the constituent molecules to be disturbed, the change will take place only in such parts of the thin lamina as are illuminated; and thus an *invisible* image formed by the shaken compound may be impressed if the time of exposure be short, or the change produced be such as not to be within the scope of our vision. Otherwise upon long exposure a *visible* image may be produced, the resulting compound being different in appearance from the original.

As the point is of great importance, we must again direct attention to the fact that the two images are exactly alike in chemical composition, one differing from the other solely in the number of molecules altered. Fortunately, methods exist of rendering visible to the eye what is ordinarily and primarily invisible, and this operation is termed the development of the image. The invisible image is frequently termed latent, an appellation which, though convenient, is yet open to some criticism. We will now discuss the various ways in which development may be effected.

1st Method.—The new compound may possess an attractive force. If a rod or wire of zinc be placed in a solution

of lead acetate, chemical operations immediately commence. The outside particles of the zinc enter into combination with the acetic acid of the lead acetate, and particles of lead are deposited upon the rod in their stead. As the action continues the lead further reduced is, by a certain well-ascertained law, attracted to the lead already deposited. Spangles of the metal in a crystalline form attach themselves to the rod and then to one another, until what is known as a lead tree results, just as a magnet will sustain a string of nails suspended from one of its poles. In a similar way a silver tree may be formed from a solution of its salts, provided the reduction be slow. So the action of light on certain sensitive compounds, especially amongst which may be mentioned those of silver, is to cause the formation of a body which is capable of attracting the metal (of which it is itself a salt), when slowly deposited from a solution. This first deposit is capable of attracting still more of the metal, and thus an image is completely built. This action is more fully treated at p. 39.

2nd Method.—The altered compound may be able to effect a reduction to a metallic state of a metal from a solution of its salt, which the original compound may be incapable of doing. In this case the metal would be naturally precipitated on the altered compound, and the attractive force of the freshly deposited metal would determine the attraction of any other that might be caused by extraneous causes to deposit itself. In this method, as in the last, it is evident that the minutest portion of the altered compound is able to effect a building up of the image.

3rd Method.—The image may be formed by the partial reduction, to a more elementary state, of the altered compounds, when treated with certain solutions, which reduction in the original compound was impracticable; also in this reduced state it may exercise the same attractive force as above. We shall have an example of this in alkaline development.

4th Method.—The altered compound may be capable of forming a coloured body when treated with metallic or other solutions. In this case it is manifest that the image must be due solely to the amount of the sensitive salt originally altered in composition, and its vigour must consequently depend upon the time the light has acted. Of this method of development we shall have examples in the more sensitive ferric salts.

5th Method.—The attractive force of an altered molecule may be utilised by causing metallic or other vapour to condense upon it in preference to the neighbouring molecules which may not have been changed by light. This first condensation may determine the following condensation. Of this we have an example in the development of the daguerreotype plate.

6th Method.—The alteration in the compound may be shown by its incapacity to absorb moisture.

7th Method.—The new compound may be incapable of entering into solution, though the original compound may be readily soluble.

The chemical agents which are utilised in order to allow the development of the latent image to take place will be discussed as each method is brought under particular consideration. It is to be remarked that these agents are technically called developers, a term which, critically speaking, is a misnomer, as in the majority of cases the part they play is a secondary one, and one which they fill whether applied to development or not. The term is convenient, however, and will be adopted in this work, though the student must in his own mind make the reservation indicated when coming across the term.

Intensifying an image already developed or visible is a term applied to a process whereby the image is (1) rendered more visible to the eye, or (2) rendered more absorbent of, and therefore less transparent to, some particular kind of light, be it white, blue, red, yellow, &c. Both of these results

can be obtained by following the methods indicated for developing the image. Fuller information regarding the necessary procedure will be given as various processes are described.

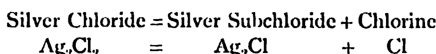
Fixing an image is rather a vague term. It is intended to express that the image due to the first exposure and subsequent development shall be so treated as to undergo no change, leading to obliteration. This is usually effected by clearing the image of all that portion of the sensitive compound which has not been acted upon by light, and thus of rendering it incapable of being obliterated by fresh exposure or appearing indistinct. If the sensitive compound were absolutely colourless, and the action of light were to leave the new compound colourless, the *developed image* would need no clearing or fixing; but, since all the sensitive compounds are either coloured themselves, or are converted by light into others possessing colour, there is evidently no safety, except in their entire removal.

CHAPTER IV

THE ACTION OF LIGHT ON VARIOUS COMPOUNDS

THE action of light on various substances must have been a matter of remark from the earliest times. The tanning of the skin, the fading of colours, must all have been noted long before an attempt was made to ascertain the cause of such alteration. However, as we pointed out in the historical sketch, silver chloride was the first substance whose behaviour was philosophically examined; and we propose to study the principal silver compounds before proceeding to other sensitive bodies. Scheele, as we have seen, found that chlorine was given off during exposure from the chloride, and that after treatment of the blackened body

with ammonia, metallic silver was left behind. There is not much need to carry the investigation further than Scheele, only the conclusion that he accepted, viz. that metallic silver was separated at the time of exposure, should be viewed with much doubt, particularly when it is found that the darkening action of the chloride takes place even when immersed in the strongest nitric acid. The accepted theory seems to be that exposure to light reduces any chloride to the state of subchloride, thus :



Silver Chloride = Silver Subchloride + Chlorine

$$Ag_2Cl_2 = Ag_2Cl + Cl$$

When the same compound is moistened the reaction appears to be different, as chlorine decomposes the water with which it is in contact, forming hydrochloric acid (HCl) whilst the other atom of hydrogen and the oxygen atom in the molecule of water combine with another atom of chlorine to form hypochlorous acid (HClO). If, instead of exposing the silver chloride in a dry state or in the presence of moisture, it is exposed in presence of free silver nitrate, fresh silver chloride is formed, and this same compound of chlorine and oxygen liberated ; and it is found generally that the darkening takes place much more rapidly when any body which will take up the chlorine is in contact with it. Thus, stannous chloride will cause more rapid darkening, from the readiness with which it absorbs chlorine. The student would do well to repeat the experiments of Scheele and those subsequently indicated, in order to convince himself that these reactions really occur. The easiest method of procuring pure silver chloride is to precipitate it from a solution of silver nitrate by an excess of pure hydrochloric acid, and to wash it thoroughly by decantation, repeating the washing to such a point that the supernatant water shall no longer show acidity when tested with blue litmus paper. This method of procedure prevents the possibility of contamination by the organic matter of filter paper. The silver

chloride, if required in a dry state, should be dried in the dark over a water-bath, in a watch-glass or porcelain capsule. A test-tube is a convenient vessel in which to give the exposure to the light, and the subsequent washings are conveniently carried out by simple agitation and pouring off the liquid. It may be noted here that perfectly dry silver chloride when exposed to light *in vacuo* remains white. This is probably due to the absence of a second substance in the tube, and a consequent inability to be decomposed. It must ever be remembered that there is no experiment properly carried out, with a set object in view, which is not worthy of record. The most trivial deviation from the expected results of an experiment often causes some new line of thought to be taken up, and may suggest important investigations.

The next silver salt that requires a careful study is the iodide; and it is owing to certain peculiarities in its behaviour when exposed to light that so much difficulty has arisen in defining the true changes that take place in it.

Silver iodide may be produced in two or more ways. The most common is by treating a silver nitrate solution with a soluble iodide, such as ammonium. If the former be in excess, even in minute poportions, after most careful washing, it will be found that the compound darkens slightly on exposure to light, whilst if the latter be in excess, there is no apparent change in colour. To explain this last phenomenon is somewhat difficult, but it must be remembered that even with the most thorough washing any salt which may have been in excess cannot be really eliminated. The iodide of the alkali is itself sensitive to light, liberating iodine, and it seems probable that, both being acted upon by light, there is merely an interchange of iodine atoms. Also it must be borne in mind that, whilst chlorine and bromine are gaseous at ordinary temperatures, iodine is solid, and cannot, therefore, so readily escape. There is also reason to believe that the molecules of iodine are more complex than

those of the other halogens, and we can thus understand that a difficulty exists in causing it to change. The shocks which will break up the chlorides or bromides are insufficient to produce any alteration when nothing but pure iodide is present.

When, however, there is an excess, however slight, of silver nitrate, the conditions are quite altered; for then there is a compound at hand which is ready to seize any iodine which may be brought near it. Thus, when the silver nitrate is present, the molecule of iodide is at once changed in chemical composition, and a subiodide is formed in a similar way to the formation of subchloride from the chloride.

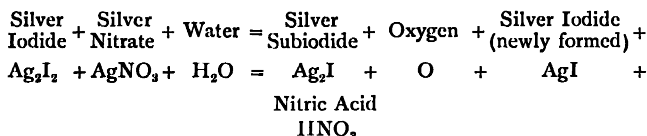

Silver Iodide = Silver Subiodide + Iodine

$$Ag_2I_2 = Ag_2I + I$$

It may here be remarked that in one respect iodine is unlike chlorine in behaviour; it is incapable of forming hypoiodous acid (HIO), though chlorine, as already pointed out, forms HClO; hence there is some difficulty in ascertaining theoretically the exact reaction which takes place between the liberated iodine and the silver nitrate which is necessarily present to produce the change.

A simple experiment, however, which it is well to repeat, throws light upon it. Take washed silver iodide, and place it in a test-tube containing in solution silver nitrate which has previously been thoroughly boiled in order to expel any air which it may contain. If an air-pump or an exhausting syringe be at hand, the boiling may be dispensed with, and the same end attained by creating a vacuum in the tube. Now expose to light; in a short time bubbles of gas will be found collecting in the solid iodide, and with care these may be collected, and on testing by the ordinary means will be found to contain oxygen. From this we may suppose that the liberated iodine decomposes the water in contact with it (as does chlorine), and produces hydroiodic acid (HI) and oxygen.

The former combines with the surrounding silver nitrate, and we have a total reaction, as follows :



Silver Iodide + Silver Nitrate + Water = Silver Subiodide + Oxygen + Silver Iodide (newly formed) + Nitric Acid

$$Ag_2I_2 + AgNO_3 + H_2O = Ag_2I + O + AgI + HNO_3$$

If any iodine absorbent be placed in contact with washed silver iodide, prepared with an excess of soluble iodide, the reaction that takes place is apparently more simple, the iodine atom combining directly with such a body. It may thus be stated as a law that *in order to produce a change by the action of light in silver iodide, some body must be present which can absorb iodine.*[1]

There are one or two suggestive experiments which may impress this on the mind. The first is to silver a glass plate as if for a mirror, and then to expose it to the action of iodine vapour (as in the daguerreotype process) to such a degree that the whole of the extremely thin film of metal is converted into iodide. On exposing such a plate to sunlight no change is visible, nor can one be brought to the cognisance of the senses by bringing developing agents in contact with it. If the film be not wholly converted into iodide, this result will not occur, as the metallic silver is an iodine absorbent. Another experiment, which is very conclusive, is as follows : Prepare a film of silver iodide, as in the wet process, and immerse it in potassium iodide solution till any excess of silver nitrate is converted into silver iodide, and wash thoroughly for an hour, and dry. Next take a small square piece of silver leaf and apply it to one portion of the iodide surface, brushing it well down, in order that real contact may be obtained. To another small portion apply a solution of tannin in alcohol, and after drying

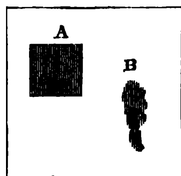
[1] This law seems to have been first emphatically enunciated by Vogel, though a claim has been made by Poitevin.

expose the plate to the light. On developing, as indicated at p. 52, a darkening action will be apparent after a short interval of time on those portions of the plate treated with the silver leaf and the tannin.

The action will be most intense in the latter, as might naturally be expected, the whole thickness of the iodide being in the one case brought in contact with the absorbent, whilst only those particles which form the surface are brought in contact with it in the latter. The experiment is more telling if the plate be exposed behind a negative, with the uncoated side next the image.

If instead of the silver leaf a thin silvered plate be pressed into firm contact with a sensitive collodion film, prepared as above, it will be found that even a fair exposure is sufficient to cause the formation of an image on both, which, though unrecognisable to the senses, is yet capable of being developed by the proper methods. This experiment thus serves to show conclusively that iodine is liberated by the impact of light; for, were the change one merely of molecular arrangement (as many inquirers have held to be the case), no image could be formed on the metal plate, the possibility of developing an image on it being dependent on the presence of silver iodide (see the daguerreotype process).

FIG. 7.



The behaviour of silver bromide is similar to that of silver chloride; hypobromous acid being formed under similar circumstances to those in which hypochlorous acid is produced. The chloride and bromide are both soluble in ammonia (which is an important point when dry plate processes are considered), whilst the iodide is not. It may be here recorded that with the chloride and bromide, as with the iodide, the presence of silver nitrate increases sensitiveness to a very high degree.

Besides the salts already mentioned there are other

inorganic compounds of silver, such as the fluoride, phosphate, silicate, which are altered by the action of light, but these are comparatively unimportant. There are, however, certain organic compounds formed, the action of light upon which can only be briefly noted here, though a fuller description of the phenomena will be given in a subsequent chapter.

When organic matter is brought into contact with a soluble salt of silver, a definite compound is often formed, and the effect of impact of light upon this is somewhat complex to trace. Thus, if we form an albuminate of silver by bringing a solution of silver nitrate in contact with one of albumen, and expose it to light whether there is an excess or defect of the silver salt present, a darkening of the compound results.

The blackened compound is not a true silver oxide, though chemical considerations lead us to infer that the coloration is dependent on the formation of silver oxide, in combination with organic matter. The same results are obtained if gelatine or other kindred body is substituted for albumen. It will be as well if the student experimentally compare the effect of light on an organic silver salt with that on silver chloride, as both are employed in the silver printing process.

The following experiments will naturally suggest themselves. Take sodium chloride and dissolve in water and add an excess of silver nitrate to it, by which we have precipitated silver chloride formed ; also take the same solution and allow the sodium chloride to be in excess. Carefully spread the moist chloride on pieces of glass, and expose to light. Both will readily darken, more especially the former, which will gradually assume an inky black tint, whilst the latter remains a pale violet. From what has already been said, the cause of this phenomenon will be apparent, the chlorine liberated in the first case is rapidly absorbed, whilst in the second it is merely held in solution, clinging as it

were to the silver subchloride, and ready to reduce it back to the same state as before. If to the silver chloride, in which the sodium chloride is in excess, we now add a little stannous chloride which is ready to absorb chlorine, the blackening will proceed as rapidly in the one case as in the other. Now treat all these residues with nitric acid, and they will all be found to remain unattacked by it, but instantly yield to a strong solution of sodium hyposulphite, leaving metallic silver in small quantities behind. Next precipitate albumen in excess, or otherwise of silver, and expose to light; the darkening will proceed more rapidly and to a greater depth in the one case than in the other. Treated with ammonia but little alteration is visible, but on applying nitric acid, the oxide at once disappears. If, however, it be treated with sodium hyposulphite, it will remain nearly unaltered in appearance. Next treat the undarkened albuminate of silver with hyposulphite, and it will dissolve, leaving a milkiness in the solution; on further adding ammonia to the solution, however, this will disappear entirely. If both the darkened bodies are treated, after the sodium hyposulphite has been applied, with a solution of hydrogen sulphide (H_2S), the former will blacken from the formation of silver sulphide, the latter will bleach from the formation of a new organic compound; the bearing of this experiment will be seen when we consider the fading of silver prints.

Again, to a similarly treated precipitate of chloride and albuminate add potassium cyanide; the one will be but slightly acted on, whilst the other will be speedily attacked. In determining the fixing agent to employ in silver printing, this point has to be taken into consideration. If experiments with other organic bodies be carried on in a similar manner, it will be found that the same phenomena will be observed; the distinction between the nature of the reduced organic compound will be seen in the different colours they assume.

From these simple experiments, then, we learn that the darkening action of silver chloride is aided by the presence of a chlorine absorbent; that the subchloride thus formed is unaltered by nitric acid (in fact, the darkening action takes place as rapidly in the presence of nitric acid with silver nitrate as if the latter be alone in excess); that the subchloride is split up by sodium hyposulphite into metallic silver and silver chloride, the latter being destroyed by it as shown at p. 56; that in organic matter which forms a compound with silver nitrate, when acted upon by light, the silver is reduced to a state of organic oxide, and that the presence of an excess of silver nitrate is not absolutely necessary; that the darkened compound is unaffected by sodium hyposulphite; that potassium cyanide is a solvent of this oxide, and not of the metallic image formed from the subchloride.

The next metallic salts to which we shall refer, in regard to their behaviour when exposed to light, are those of iron and uranium. Their reactions are almost precisely similar. To Sir John Herschel we owe most of our knowledge of the iron compounds; whilst to Niépce de St. Victor is probably due the discovery of the particular properties of uranium. If we brush over a piece of paper a neutral solution of ferric chloride, and, after allowing it to dry, expose it to light, the yellow colour imparted to it will be found gradually to disappear, leaving the surface apparently bleached. If, now, we allow a solution of potassium ferricyanide to flow on to the exposed paper, it will be found that a deep blue coloration is immediately produced, whilst if applied to the unexposed paper no such phenomenon would be observed. From chemical experiment we know that, in order to produce the blue precipitate, it is necessary to have in contact with the potassium ferricyanide some ferrous compound. Since it was a ferric compound, viz. ferric chloride, which was applied to the paper, we are led to conclude that the action of light has been to reduce this salt to the state of ferrous chloride.

By similar experiment we become convinced that the action of light on all ferric salts, ***under certain conditions***, is to reduce them to the ferrous state. It may be remarked that in order to produce the requisite reduction, the presence of organic matter, such as the size of the paper, with some of these iron salts seems a necessity; if this be absent, the action is very slow. And, again, the organic compound should be of such a nature that it is ready to combine with the atoms thrown off, in the same way as that already indicated for silver iodide. There are a variety of bodies which will combine with these atoms; but unfortunately, as a rule, they have a greater affinity for the atoms than has the iron compound with which they are only loosely combined. The organic matters with which they will combine without being torn away from the iron are rather slow absorbents, and therefore generally the sensitiveness is not great. For, as with the silver iodide, the sensitiveness depends chiefly on the readiness of the neighbouring matter to absorb what is thrown off.

In order, then, for iron salts to become as sensitive to light as silver salts, some body must be found which, *per se*, will not reduce them to the ferrous state or decompose them, yet which, when the atom is liberated, will seize it with greater facility than any body with which we are as yet acquainted. As a rule, the development of these pictures is carried out by either method 2 or 4 (pp. 19, 20), the details of which will be given in the section on printing with these salts. Since these compounds are comparatively but little sensitive to light, they are chiefly used for obtaining positive prints; an exposure in the camera to produce a developable image would have to be very prolonged.

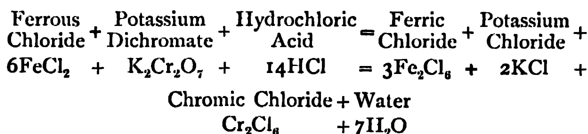
The same experiments carried out with regard to the uranium compounds give identical results. The uranic compounds are reduced to uranous, and the methods of development are similar.

To the same class of metals belongs vanadium, the

interesting compounds of which were investigated by Professor Roscoe. The reactions are similar to the above.

The last metallic compounds to which we shall refer at length are those of chromium combined with the alkalis.

The salts found most sensitive to light are the dichromates, though the chromates are also, to a certain extent, capable of being acted upon. Mungo Ponton first indicated the principle which governs their employment. If a solution of a dichromate, such as that of potassium, be brushed over paper, and be allowed to dry, and be then exposed to light beneath an engraving, it will be found that in those portions corresponding to the white paper the orange colour will gradually assume a delicate brown tint, whilst on the parts shaded by the lines the salt remains unchanged. The eye then at once tells that some chemical change has taken place in the chromium compound. Chemists are accustomed to employ the dichromate to convert a ferrous salt into a ferric, and by having it in a solution of known strength, and ascertaining when the reaction is complete, the amount of iron in the ferrous solution can be estimated quantitatively. Thus we have, say, the amount of ferrous chloride to test quantitatively : the amount is calculated by applying the following equation :

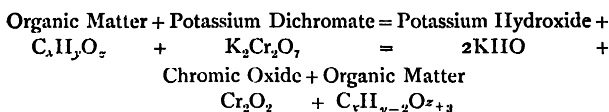


Ferrous Chloride + Potassium Dichromate + Hydrochloric Acid = Ferric Chloride + Potassium Chloride + Chromic Chloride + Water

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 3Fe_2Cl_6 + 2KCl + Cr_2Cl_6 + 7H_2O$$

It will be seen that the potassium dichromate readily parts with its oxygen and potassium, and becomes converted into a pure chromium compound. The change induced by the light is analogous to this, there being every reason to believe that the following equation is a type of the reaction,

though carbon dioxide may be a product to form potassium carbonate—



Organic Matter + Potassium Dichromate = Potassium Hydroxide +

$$C_xH_yO_z \quad + \quad K_2Cr_2O_7 \quad = \quad 2KHO \quad +$$

Chromic Oxide + Organic Matter

$$Cr_2O_2 \quad + \quad C_xH_{y-2}O_{z+3}$$

An analogous reaction of a chromium salt in the presence of an organic compound, without the impact of light, is found in chromium trioxide. If alcohol be dropped on these dry crystals, oxygen is evolved so rapidly that the spirit is ignited by the energy of the act of combination. Now the dichromate contains less oxygen than the acid (H_2CrO_4) formed by the trioxide (CrO_3), hence the evolution of oxygen from it is likely to be less easily effected by organic matter than from the latter. The swing caused by the waves of light is sufficient to effect the change that is indicated by the equation above. It will be noticeable that not only is the chromium compound altered in composition, but that also the organic matter is deprived of hydrogen; and it is the fact of this deprivation, or change in organic matter, that renders the dichromates valuable for photographic purposes. It will be found, after experiment, that the dichromatised paper prepared as above is nearly insensitive when moist, and that the image can be formed most readily when it is dry. The reason of this is probably that when dry the organic matter and dichromate form a real compound, which is, however, readily split up on remoistening. If, however, the contact be long continued, an alteration in the position of the atoms of the molecules probably commences. This might account for the insolubility of old carbon tissue, and it may be presumed that the change which is rapidly effected by light is much more slowly accomplished by the long contact even in the dark.

The development of pictures taken on ordinary sized paper is usually effected by method 4 (p. 20), and will be noticed when treating of the aniline process. When,

however, the paper is coated with a layer of organic matter, such as gelatine or albumen, the development of the picture may be effected by methods 6 or 7. Colloidal bodies available for photographic purposes, when oxidised, are changed in physical as well as in chemical properties. 1st, they cannot after oxidation be dissolved by water, either hot or cold, though before oxidation they may be easily soluble. 2nd, they will not *absorb* water, and consequently will not increase in bulk, if the impact of light be prolonged. These modes of development will be entered into fully when treating of the carbon and collotype printing processes.

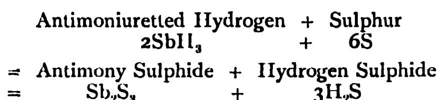
It is scarcely necessary to refer to the salts of other metals; they are mostly too insensitive to the action of light even for contact printing. Robert Hunt, in his excellent 'Researches on Light,' has entered fully into the phenomena observable with most of these compounds, and the student should study that work for further information.

Of organic bodies there are a variety which respond to the chemical vibrations. First and foremost, as being of practical utility, is the substance known as asphaltum, or bitumen of Judæa. It is the substance which was first employed by Niépce for practical photography, and it still retains its place amongst useful photographic compounds. It is readily soluble in a variety of menstrua, such as benzole, chloroform, and turpentine. After exposure to light, it loses its excessive solubility, and it is not only possible, but practicable, to dissolve away from a thin layer of it all those portions which have not been acted upon by light. For certain photo-engraving and relief-printing processes it is still employed, on account of its resistance to the action of acids (see p. 246). It seems that during exposure it becomes oxidised to a certain extent.

Amongst other sensitive organic compounds may be named the extracts of flowers and leaves and certain dyes. The sensitiveness of these last has recently been found to be of use in what is known as ortho-chromatic photography.

Among gaseous bodies which are sensitive to light we may name chlorine, when exposed in the presence of hydrogen. If in a dimly lighted room the proper combining volumes of these two gases be mixed in a glass bulb, or other convenient holder, and then exposed to the direct rays of the sun, or other strong source of light which emits the shorter wave-lengths, it will be found that they combine with explosive violence to form an equal volume of hydrochloric acid. In diffused daylight the combination takes place much more quietly, and attempts have been made to utilise this action to measure the 'actinism' of any light to which it may be exposed (see 'Actinometry'). The affinity of chlorine for hydrogen is so great that it causes a decomposition of the water in an aqueous solution, when exposed to the light, though it has no power to do so if kept in the dark.

The discovery that light will cause a combination between a gas and a solid is due to Mr. Francis Jones, of Manchester. He found that in sunlight, if sulphur was brought in contact with antimoniuretted hydrogen or stibine, the orange sulphide of antimony was formed. The equation representing the reaction is as follows:



Antimoniuretted Hydrogen + Sulphur
$2SbH_3 + 6S$
= Antimony Sulphide + Hydrogen Sulphide
$= Sb_2S_3 + 3H_2S$

With arseniuretted hydrogen (AsH_3) a like reaction takes place.[1]

After this brief *résumé* of the sensitive compounds the student will at once distinguish the advantage to be gained by the employment of the simpler salts of silver for obtaining images in the camera. It is these alone which are susceptible of rapid development by exercising an attractive force when the altered molecules are few in number; whilst all the other compounds require a large number of particles to be changed in order that the image may be made visible

[1] As being substituted for Sb in the above equation.

at all. With the iron salts *per se* the development by attraction may be resorted to; but it will be found on experiment that the attractive force is so small that it does not nearly equal that of the silver compounds. Hence we may assert that, for producing developable images in the camera, the chief portion of the sensitive salt must consist of one of these silver salts, and that other metallic salts can best be utilised for obtaining impressions by long exposure, and are therefore chiefly adapted for obtaining positive proofs from negatives.

CHAPTER V

ON THE SUPPORT AND SUBSTRATUM

In judging of the kind of support on which to receive an image, whether it be developed or formed by the continued action of light, it must be considered for what purpose the image is to be employed. If it is to be employed as a screen, or a negative from which to form a picture complementary to it in photographic density and position, then evidently the more transparent the support is, the better it will be for this particular purpose. As a rule, it is only images impressed in a camera which are employed as 'negatives,' and as these may be said to be invariably taken upon the sensitive salts of silver, which are easily acted upon chemically by extraneous matter, it is evident that a substance should be employed which is unaffected by them and by the agents which cause the development of the image. In addition to this quality, a certain amount of rigidity in the support is convenient, though not essential, as the operations involved are of such a character as to cause this to be a desideratum. Evidently glass answers the object most thoroughly. Less fully does paper when waxed answer these requirements; for with it there is translucency and not transparency, and none of the other qualities.

The Kodak Company use as a support a band of thin transparent celloidin. It is adapted for use in a roller slide.

A stouter transparent support of celloidin is also used to hold the sensitive gelatine film, which takes the place of glass in the ordinary dark slide.

To give a correct idea of an image by reflected light, that is, to look at it as a picture is looked at, it should appear as highly coloured or as black as possible when contrasted with the ground on which it rests. Formed by development (after exposure in the camera), it possesses always more or less density, the density *approximately* varying inversely as the intensity of the reflected actinic light which has acted on it. If the developed image be of a dark colour, the proper effect of light and shade will be reversed. To give a correct representation, the deposit must be *transparently white*, and the support dark-coloured or black. In the daguerreotype process the support is a metal plate, which is by contrast dark when compared with the mercurially developed image. In the collodion process, if the image can be made to appear white by reflected light, the support may be of glass, if it be backed with some dark-coloured substance, such as black velvet or varnish, or it may be of metal darkened with some substance that is unaffected by the chemical agents employed (an example of this we have in the ferrotype plates). On the other hand, if the picture be produced by a subsequent operation from a negative, the image should be as *transparently dark* as possible, and the ground white. In this case the support (unless other considerations forbid it) may be white paper, opal glass, or any other white medium. It is also worthy of notice that in order to produce a proper representation of light and shade the ground should always be in contact with the image. An example of a certain false gradation given in an image, in which this important rule is neglected, is to be found in the old collodion positives on glass.

Heretofore nothing has been said regarding the vehicle

employed for holding the sensitive compounds *in situ* on the support, and this requires a detailed consideration. It need scarcely be said that some sort of vehicle is generally necessary. The fact that most of the compounds employed for photographic purposes are solids, and whether formed by precipitation from or evaporation of a solution are in a pulverulent state, at once clearly demonstrates the necessity. We must distinguish between two cases.

1. In the case in which the image is formed by development, it is essential that the developing agent should cause no chemical change or discoloration in it any more than in the support. Now the sensitive compounds may be formed in the support itself. Thus a solution of potassium bromide brushed on to paper, and then followed by a similar application of silver nitrate, will cause the formation of silver bromide in the paper. The paper will in this case act as a support and vehicle too. An invisible impressed image can be developed on it, but it would be found that it is liable to stains due to the organic matter of the sizing. It is also only translucent and not transparent. And it is therefore, as a rule, unadvisable to use it for holding the sensitive compounds *in situ* when 'negatives' are required. Again, if the support be not at the same time a medium, it is essential that the latter should adhere to the former during the operations of development.

2. When the image is to be formed entirely by the direct action of light the above conditions are not a necessity. Then paper will be suitable for a medium, as there is nothing extraneous to the sensitive compound to act upon it. At the same time there is nothing to forbid the employment of all other vehicles which are not acted upon by the sensitive compound. In the production of camera pictures collodion was, till some twenty years ago, alone[1] employed; and it is particularly suitable for holding precipitable silver compounds in position, as it is a ready solvent of most of the

[1] For exception see the gelatino-bromide process.

bodies which it is necessary to use, and the precipitation can be effected in the viscous collodion itself. The silver compounds are thus formed in a finer state of division than they would be if precipitated from an aqueous solution. This point is most important, for light impacts upon surfaces; and as the surfaces of similar particles increase as the square of the diameter, whilst their masses increase as the cube, it is evident the smaller the particles are the larger will be the available area for the same quantity. Collodion is a transparent, semi-viscous fluid, made by dissolving pyroxyline (gun-cotton) in a solution of ether and alcohol, and is for ordinary purposes totally unacted upon by the sensitising solution of silver, though, when specially prepared, it is believed that an organic compound of silver is formed. Other advantages of collodion are to be found in the property it has of setting in a gelatinous form, previous to its final desiccation, and also that the solvents used evaporise rapidly at ordinary temperatures, leaving the salts, which are to form the precipitate, if not in solution, yet with their individual particles in such an extremely minute state of division as to be undistinguishable to the eye.

Aqueous solutions of gelatine and albumen are equally good solvents of the salts alluded to. When, however, gelatine is employed, as in the gelatino-bromide process, the direct combination between it and the silver is avoided.

CHAPTER VI

DEVELOPMENT OF THE PHOTOGRAPHIC IMAGE

THE importance of a thorough understanding of the rationale of developing an image in the silver compounds is not to be overrated, as a close study of it furnishes clues

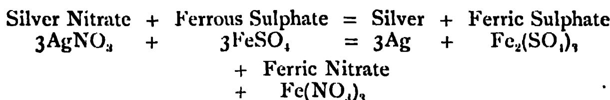
to apparently mysterious results, which are so often met with by every student in the art. The method of developing the Daguerrean image is given in chap. xiii., and we propose in this chapter to confine ourselves to that employed in what is known as wet-plate photography and dry-plate photography, and also that followed in the calotype and other kindred processes.

It will be recollected that by method 1 the invisible image was to be made visible by the attraction exercised by the new compound formed after the impact of light on the original one. As already announced in chap. iv. p. 24, the change effected on a molecule of silver haloid is its reduction to a lower type, *i.e.* one containing a lesser number of atoms. Thus Ag_2I_2 was reduced under certain circumstances to Ag_2I, the other atom of iodine being absorbed by some body in contact with it. A similar change was shown to be effected on the silver bromide and chloride. We may therefore take as a type any one of these. We will choose the iodide, and follow the development from the earliest stage, when used in the wet process.

It has already been shown at p. 19 that the building up of the image is due to the well-recognised law that every minute freshly formed crystal attracts every other of a similar nature, and that the formation of the tree is entirely due to this molecular attraction, and the slow reduction of the metal from its solution. If the metal were deposited rapidly the same law would still hold good, but the attraction of one reduced molecule on its immediate neighbour would be greater than that exercised by the metal adhering to the rod, as the probable distances in the one case would be far less than in the other. A particle of such a size and weight would therefore be built up before the metal on the rod could draw it sufficiently near to overcome the force of gravity exercised on it ; hence it would sink to the bottom of the containing vessel.

If we take a solution of silver nitrate and add to it a

solution of ferrous sulphate, we have an almost instantaneous reduction of metallic silver. Thus—



$$\begin{array}{ccccccc} \text{Silver Nitrate} & + & \text{Ferrous Sulphate} & = & \text{Silver} & + & \text{Ferric Sulphate} \\ 3AgNO_3 & + & 3FeSO_4 & = & 3Ag & + & Fe_2(SO_4)_3 \end{array}$$

$$+ \text{ Ferric Nitrate}$$
$$+ \quad Fe(NO_3)_3$$

Any other oxygen-absorbing medium which is incapable of causing double decomposition with the silver nitrate might be substituted for the ferrous sulphate. By adding an acid to the latter the same action takes place, but much more slowly, the time necessary to effect the total reduction being dependent on the amount of acid present. Supposing by some means or another we are able to cause the first crystals of the silver to deposit themselves in certain positions, we may be sure from analogy that the remaining crystals will adhere to these and build up a miniature silver tree. In the wet process, and also in the dry, we have means of causing these first particles of silver to deposit on the invisible image.

This invisible image is formed of subiodide of silver (Ag_2I). Only one of these atoms of silver is saturated ; the other is still ready to combine with any other atom with which it has an affinity. Such an atom it finds in freshly deposited silver. The solution of silver nitrate is already present in the wet process, and in the dry processes it is added to the oxygen-absorbing agent, which is employed in both.

The first deposited crystals attract others, and thus an image is built up. It may, however, be asked how it is that different density of deposit is caused. The answer to this is that the invisible image is formed of variable quantities of the subiodide, approximately proportional in fact to the intensity of light acting on it. At any spot on the sensitive surface it is the integral of the attractions of the different atoms lying close to one another that determines the amount of the first

deposit, and the varying mass of this determines the distribution of the subsequent deposit.

It is an axiom that the stronger the solution of the reducing agent the more rapid must be the deposit, and it may be convenient here to discuss the bearing of this. Suppose adjacent particles of the sensitive surface possess separate attractions of, say, 1, 2, 3, and 4 units, caused by the different intensities of light acting on those parts. The probabilities are that the first metallic silver atom deposited will be drawn to the spot possessing 4 units of attraction. If the interval in time for the reduction of the next atoms exceed that necessary for placing the first atoms *in situ*, the attraction originally equal to 4 units will become approximately 5, and the probabilities are that the larger proportion of the next reduced atoms will be attracted by the 5 units than by the 3; and by the same action the 4 units may attract several atoms, whilst the 3, 2, and 1 units may have attracted proportionally less. If the reduction of a sufficient number of atoms to saturate the whole of the atoms of Ag_2I take place almost simultaneously, the probability is that the difference in the increase of attractive power will be less marked. Thus 4 may become 5; 3, 4; 2, 3; and 1 become 2. It may therefore be asserted that the position of the first deposition will determine that subsequently taking place, provided the same rate of the reduction be maintained. From the foregoing reasoning it will be apparent that the stronger the developing solution the less marked will be the variation in density due to the different intensity of light acting on the various portions of the sensitive salt.

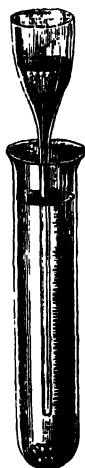
The more viscid a liquid and the smaller the mass of the particle, the more slowly will a particle travel through the liquid. An application of this law has been made to development. A certain amount of colloidal substances, such as gelatine, albumen, or these bodies acted upon by acids, is added to the liquid in which the oxygen-absorbing agent is

dissolved. Though the reduction of the silver nitrate to the metallic state may take place as rapidly as in a solution in which the colloidal body is omitted, yet the time the metallic atoms take to travel through the viscous solution is lengthened to such an extent that an appreciable time is taken to form a visible particle of silver. The time, therefore, taken to build up an image is longer than with a solution in which the colloidal substance is absent; it is found that a small quantity of the colloid will give sufficient viscidity to cause slow deposition. The examination under the microscope of an image developed in the manner indicated above will perhaps throw more light on the subject than any verbal description that can be given. It will be found that the whole of the image is formed of these minute crystals, varying in size according to the length of time which they took to deposit. The appearance of the film when the half-tones of the negative are thus examined will be as though it had been sprinkled with the metallic granules by means of a pepper-box; whilst the parts representing deep shadows will be represented by large patches of bare collodion, with here and there a crystal lying embedded in the film. The student should take every opportunity of studying the effect of different kinds of development as regards the actual physical composition of the image; and he may rest assured that the highest excellence in any negative can never be attained when the deposit is coarse and highly crystalline.

As we proceed to the practical part of dry-plate processes, it will be found that the sensitive salt which is principally employed is the bromide of silver. Sometimes the silver bromide has a large proportion of iodide in combination with it and sometimes chloride, but it may be taken as an axiom that the really effective salt of silver is the bromide, though the conditions of sensitiveness may be altered by the presence of either or both of the other two salts. In the development of dry plates by what is known as the alkaline method, instead of the image being built up from

a silver salt external to the film, it is built up from the solid silver salt in the film itself. The iodide is very feebly amenable to this treatment, but the bromide and the chloride are readily acted upon by the developing agents. These agents are in reality compounds which have a strong affinity for oxygen. Pyrogallic acid and its congeners, in combination with an alkali, are those most usually employed, though in some quarters, more particularly on the Continent, the organic ferrous salts are in equal favour. The behaviour of the alkaline pyrogallic acid is almost precisely similar to that of the latter salts; and any argument or experiment that is applicable to the one is also applicable to the others.

FIG. 8.



The following experiments should be made by the student, that he may become acquainted with all the phenomena connected with this class of development.

1. Precipitate pure bromide of silver, say 4 grammes, and wash thoroughly; then place it at the bottom of a test-tube, and cover it with a solution of pyrogallic acid (about ·3 gramme to the 100 c.c.) to within a short distance of the top. Having drawn out from ½-inch tubing a fine funnel, let him place the end drawn out just above the bromide, and then pour into the funnel 3 or 4 drops of strong ammonia. It will be seen almost immediately that a black layer forms above the bromide, that the silver is reduced, and that the action continues for a certain time, and then stops. The blackening of the liquid will be found to be due to the alteration in the pyrogallic acid, consequent on the absorption by the alkali of the bromine abstracted from the bromide.

2. Repeat the experiment, replacing the pyrogallic acid by dilute ammonia (say ·880 sp. gr. diluted with ten times its bulk of water), and drop into the funnel a small

quantity of strong pyrogallic solution. The phenomena presented will be slightly different. A cloud will instantly form in the ammonia, and if the surface of the bromide has been protected by a small diaphragm of paper, the whole of the solution may be poured off, and the surface of the bromide will be found almost unchanged. The difference is caused by the *solubility* of silver bromide in ammonium hydrate; and the portion held in solution is consequently more readily reduced than that remaining in the solid state.

3 and 4. Repeat these two experiments, substituting potassium hydroxide (caustic potash) for the ammonium hydrate. The phenomena presented in both cases will be identical; the silver bromide will be reduced from the solid state. This is because *silver bromide is insoluble in the potassium compound.*

5. The next experiment should be to dissolve a small quantity of silver bromide in ammonia, and then drop into the solution a small quantity of potassium bromide solution. It will be seen that a precipitate is immediately caused, which, on analysing, will be found to be silver bromide combined with ammonia.

6. Repeat the foregoing experiments with silver iodide, first with weak solutions, and then with concentrated. It will be found that the concentrated will act upon the iodide, whilst the weaker will not. The iodide not being soluble in ammonia, the phenomena described in experiment 2 will not be observable.

Reviewing these experiments, we are led to the following conclusions: that the alkaline pyrogallates have such an affinity for the halogens that they are capable of breaking the bond existing between the silver and the bromide; that the portion which is soluble in the alkali is most readily acted upon; and that the addition of a soluble bromide diminishes the amount capable of being dissolved. Consequently, if a surface of silver bromide were treated with ammonium pyrogallate, we should expect that the undis-

solved bromide was less readily reduced than that portion which is dissolved, and that less immediate reduction would take place when a soluble bromide, such as that of potassium, were present.

At p. 22 we have said that the photographic image is probably a subsalt of silver. Thus that formed on the chloride will be subchloride (Ag_2Cl). With the bromide the same holds good. The action of light is to isolate the sub-bromide, bromine being liberated. Thus—

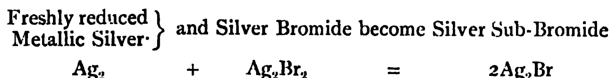


Silver Bromide becomes Silver Sub-Bromide + Bromine

$$Ag_2Br_2 = Ag_2Br + Br$$

Suppose we have a mixture of bromide and sub-bromide of silver, it is very easy to theoretically determine which compound would be first reduced to the metallic state by the action of the alkaline reagent. It is merely a question as to which requires the least work to be done on it as to which will be first reduced. In the case of the bromide of silver two atoms of bromine have to be removed before the metallic silver results, and in the other only one atom. It is evident, then, that in such a mixture as we have assumed, the sub-bromide would be the first to be reduced, and not till that had been effected would the bromide be attacked.

In the case of a photographic image on a plate before development, the amount of sub-bromide is infinitesimally small; but, infinitesimal as it is, that must be reduced to the metallic state before the neighbouring molecules of bromide can be attacked. It might be thought, as this must be so rapidly done, that the bromide also would be at once reduced. But here another phenomenon comes into play. It appears that the bromide of silver and freshly reduced metallic silver cannot exist separately in contact, but that immediately new sub-bromide of silver is formed. Thus—



Freshly reduced Metallic Silver and Silver Bromide become Silver Sub-Bromide

$$Ag_2 + Ag_2Br_2 = 2Ag_2Br$$

At any rate, an action of somewhat this description takes

place in the film. An interesting experiment is confirmatory of this. Take an ordinary dry plate, such as an albumen-beer plate, and expose it in the camera. Coat half of it with a bromide emulsion, and develop it by the alkaline method. That part coated with the bromised collodion will be found to acquire density. When dry, remove the film from off the glass plate with gelatinised paper, and also cause the adhesion of a similarly prepared gelatine paper to the surface primarily next the plate. When nearly dry, the exposed film can be split off from the bromised film; and on examination it will be found that there is an image on both films. If the sensitive salt in the collodion film exposed in the camera be iodide, an image may be developed, though it will be weak.

The fact remains, then, that this action takes place, even though the films be separated by a very thin layer of albumen. It will also be apparent that the image will be stronger when developed with ammonia than with potash, for with the former the silver can be deposited from the solution. The writer has been able to intensify images from alkaline or neutral solutions of sodium hyposulphite and potassium cyanide, in which have been dissolved silver chloride, by this action of pyrogallic acid.

The restraining action of soluble bromide (potassium &c.) is most probably due to the fact that these salts form double bromides with the silver, and not with the sub-bromide, as might be expected from chemical considerations. To reduce the double bromide to metallic silver evidently entails more work than the reduction of the silver bromide by itself, and the freshly precipitated silver has also to loosen the bond between the double bromide before it can combine with the silver bromide to form the fresh sub bromide, hence the reduction is slower. In practice this is the case. A developer in which a full dose of bromide is present develops more slowly than one in which it is present in small quantities only.

It should be noted that the same treatment of the bromide is effective when gallic acid is employed instead of pyrogallic, the power of reduction of the former being smaller than that of the latter. This fact proves that with a weakly formed invisible image a strong reducing agent should be used.

In the silver bromide emulsion plates, for which this development is particularly adapted, it will be noticed in subsequent pages that in order to obtain pictures which are free from veil or fog one of three conditions is necessary—either there must be a little soluble bromide in the film, or else if there be an excess of silver nitrate over that necessary to combine with the bromide there must be some free mineral acid or the excess must be converted into silver chloride by the decomposition of some metallic chloride present.

These conditions are apparently conducive to the formation of bright images. It will be profitable, however, to consider the probable cause of this. Bromide of silver is usually formed by the double decomposition of silver nitrate and soluble bromide, such as a proportion of potassium with that of cadmium. Cadmium and other dyad metals may form two bromides, the ordinary bromide and a sub-bromide. In ordinary circumstances the latter compound is found in very small quantities, but when it comes in contact with silver nitrate, a sub-bromide of silver, or, otherwise, bromide of silver, with unattached atoms of metallic silver, is formed. When the soluble bromide is in excess, these molecules—supposing them to be half molecules of silver bromide together with the attached atoms of silver—readily attract the excess of soluble bromide; and when these atoms of excluded silver lose their nascent power of attraction, they become incapable of causing a reduction of the neighbouring bromide when a developing solution is applied. If, however, these sub-bromide molecules remain as such, the action of the reducing agents is to attack these first, and the

reduced silver exerts its power in determining the reduction of the neighbouring molecules; in other words, causes reduction where light has not acted.

Sometimes the metallic or other soluble bromides are contaminated with minute traces of oxides; when this is the case, nitric acid converts these into nitrates. This same acid also will act upon the sub-bromide, though not on the subchloride. Thus Ag_2Br is decomposed into AgBr and $AgNO_3$; or if nitric acid be applied to the soluble bromide, such as of cadmium, before its contact with the silver nitrate, we probably have a precisely similar reaction. The addition of certain metallic chlorides produces a similar result, preventing the formation of Ag_2Br, but some acid is almost necessary when any oxide is present.

As touching the strengths of the solutions to be employed, 1st. The stronger the ammonia, the greater the amount of the silver bromide that is dissolved. If the amount dissolved be in excess of that necessary to supply a gradual aggregation of silver on those parts on which a deposit has already taken place, the result must be a veil on the whole surface.

2nd. The stronger the pyrogallic acid solution in the presence of sufficient alkali, the more rapid will be the reduction of the silver bromide; hence a strong solution is very likely to cause fog, even if sufficient soluble bromide be present.

3rd. The strength of the bromide solution must be dependent on the rate at which a picture has to be developed. A sensitive salt which has been exposed to the prolonged action of light will bear a very strong solution of bromide, the reason being that it is necessary that the double bromide of the alkali and silver should be formed simultaneously with the reduction of the sub-bromide. If this be not effected, some portion of the silver bromide will be reduced before it is protected by the formation of the double salt. (It must not be forgotten that silver bromide

is slightly soluble in the bromides of the alkalis.) There is another form of restraint to the energy of reduction by the alkaline developer which is most important in the present day—viz. a physical restraint. At p. 41 we have shown that the action of viscous solutions is to cause the slow deposit of metallic silver from a solution of silver. In a similar way colloidal substances when moist or wet prevent the alkaline developer acting so rapidly as when free. Thus, instead of a soluble bromide, it is quite feasible to use glycerine and albumen to get the sub-bromide reduced alone before the bromide itself is attacked. Time is in reality the factor we have to pay every attention to. If we can extend the time of reduction, we can make certain that the salt acted upon by light is alone reduced in the first instance, and allows the secondary action of the formation of new sub-bromide to take place before the bromide is attacked. Whether the restraint be physical or chemical, of one thing we may be certain, that such restraint implies a less energy capable of being brought into play in a certain time; and if the time be sufficiently long, the energy at any instant will be insufficient to reduce the bromide, though it may suffice to reduce the sub-bromide. If we compare the above method of development with that given in the early part of this chapter, we shall see that the latter is the only one which is feasible for the wet process, and the present one for dry processes. In the wet process there is a solution of silver nitrate on and in the film; the unbonded atom of silver in the subsalt is in a state possessing the greatest attractive activity, and development must take place shortly after exposure. If the second method were adopted, all the silver nitrate would have to be eliminated from the film by prolonged washing: in practice it is found that the resulting image is liable to be of unequal density. Again, the proportion of bromide to iodide in the collodion is small, and as the iodide is only affected by intensely strong alkaline developers, the chance of veiling the image

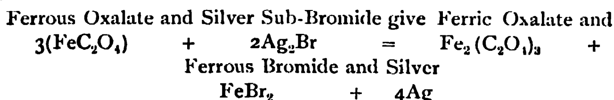
through the reduction of the bromide unacted upon by light is increased, if sufficiently strong solutions are employed to cause the reduction of the subiodide.

With dry processes the advantages rest with the alkaline method. The development takes place hours, or even months, after exposure ; consequently, if the method used in the wet process be adopted, it is quite possible that the free atom of silver in the subiodide or sub-bromide has partially lost its nascent energy, and that when the free silver nitrate, together with the developing solution, is applied to the surface of the film, the intensity of molecular attraction is diminished. The same amount of attractive power may be obtained by increasing the number of molecules acted upon by light; hence what in the wet process would be a sufficient exposure, for this development, in the dry may be totally inadequate. Besides this, in the most recent process, in which gelatine forms the vehicle in which the sensitive salt is embedded, the addition of silver nitrate is impracticable, since it would only induce stains over the whole surface and obliterate the image, even if the image could be readily developed.

Coming to the second method, however, the result differs. Even if the silver atom of the sub-bromide be inert, the agents employed will still naturally first attack the remainder of the molecule, by taking up the bromine and liberating the other atom of silver. Now this liberation takes place in close contact with another atom, and as the attraction varies inversely as the square, or more, of the distance, a much less attractive force is necessary in order to draw the liberated atom to its partially saturated neighbour. The atom once *in situ* attracts the other depositing atoms, and an image is rapidly built up. As a matter of fact, in those processes in which both methods of development are possible it is found that alkaline development causes a gain of from 4 to 50 times in the matter of shortening exposure, more particularly when a large quan-

tity of silver bromide is present from which the atmosphere is excluded by its being embedded in a comparatively thick film, as in the gelatino-bromide process.

The organic salts of iron (ferrous) have been alluded to as acting in the same way as the pyrogallic acid and alkali. It is more easy to give the chemical reactions which take place with the former than with the latter. The typical salt may be taken to be ferrous oxalate dissolved in a solution of neutral potassium oxalate. The decomposition of the sub-bromide entails an alteration in the ferrous salt employed as follows :



Ferrous Oxalate and Silver Sub-Bromide give Ferric Oxalate and

$$3(FeC_2O_4) + 2Ag_2Br = Fe_2(C_2O_4)_3 +$$

Ferrous Bromide and Silver

$$FeBr_2 + 4Ag$$

In some processes the citrate and tartrate of iron are employed. The same form of equation applies also to them.

CHAPTER VII

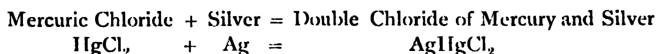
GIVING INTENSITY TO THE IMAGE

ANY method of increasing the apparent depth or blackness of the image when received by reflected light, or of increasing the opacity of the image to actinic or to visual rays, is termed intensifying the image, and in both cases the result can be brought about by the same procedure. The following are modes of giving intensity to the image.

1st. We may continue the development of the image by method 1, if we supply more free silver nitrate solution to it when exhausted ; and this will give us the necessary intensity. The theoretical considerations before noted need not be again brought before the student, neither is any special experiment necessary to impress them on his mind.

2nd. We may produce opacity to photographically active

rays by increasing the deposit by other means. As an example of what is meant, we may apply to the silver image a solution of mercuric chloride.



Mercuric Chloride + Silver = Double Chloride of Mercury and Silver

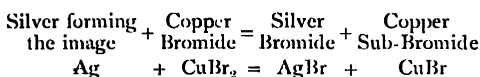
$$HgCl_2 + Ag = AgHgCl_2$$

This at first is grey (probably due to the formation of silver subchloride), but it finally becomes a pure white. It will be noticed that each atom of silver attracts one atom of $HgCl_2$. As regards opacity without regard to colour, the image must evidently be more opaque. It is, however, as regards photographically active rays much less opaque than when the image was of the grey due to the silver.

An application of ammonium hydrate to it, however, converts it into a jet black or deep brown.

Here we have a still further deposition on the silver atom, which is therefore denser, and, being black, is very opaque to actinic rays.

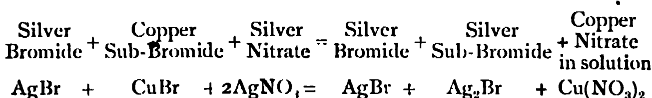
As another example of this mode of intensification we may instance the effect of copper bromide on metallic silver, and the subsequent treatment of the deposit thus formed with silver nitrate.[1]



Silver forming the image + Copper Bromide = Silver Bromide + Copper Sub-Bromide

$$Ag + CuBr_2 = AgBr + CuBr$$

When treated with silver nitrate we have--



Silver Bromide + Copper Sub-Bromide + Silver Nitrate = Silver Bromide + Silver Sub-Bromide + Copper Nitrate in solution

$$AgBr + CuBr + 2AgNO_3 = AgBr + Ag_2Br + Cu(NO_3)_2$$

It will be seen how immensely the deposit on the image is increased by this method.

Lastly, intensity in an image may be secured by substituting some other metal for the silver by chemical means. For example, we may apply a solution of platinum tetra-

[1] For a detailed account see *Photographic Journal*, April 1877.

chloride; the silver will be converted into chloride, and the platinum will be deposited in its place. The silver chloride may be subsequently dissolved away by sodium hyposulphite or ammonia, or by many of its well-known solvents.

From a study of these methods it will be apparent that methods 2 and 3 must each be carried out on an image from which everything else is removed but the metallic silver; method 1 may be employed without such removal.

The formula for the first method, which is only applicable to collodion plates, are as follows:—

No. 1.	Pyrogallic acid	4 grammes
	Citric acid	4 to 8 grammes
	Water	1 litre
No. 2.	Ferrous sulphate	10 grammes
	Citric acid	20 grammes
	Water	1 litre

With the latter intensifying solution detail in the shadows is often brought out, though absent in the development, but the former is the most efficacious for rapidly giving opacity to the image. With each of the above a few drops of a solution of

Silver nitrate	20 grammes
Water	500 c.c.

must be added immediately before application to the film. These intensifying solutions may be applied to the image either before or after fixing; those which follow, however, require the unaltered iodides and bromides to be previously dissolved away.

Iodine	·1 gramme
Potassium iodide	·2 gramme
Water	50 c.c.

The iodine (which is held in solution by the help of the potassium iodide) converts a portion of the reduced metallic silver into iodide, and when continued but for a short time the image has a bluish-green tint, which is more non-actinic

than if it were left in the metallic state. If this be not sufficient a solution of

Potassium permanganate . . .	1·5 gramme
Water	50 c.c.

may be flooded over it. The permanganate is decomposed in coming in contact with the silver iodide, and insoluble manganic oxide is precipitated on the image.

Another form of intensifier is made by

Mercuric chloride	·2 gramme
Water	750 c.c.

and,

Potassium iodide	1 gramme
Water	50 c.c.

The latter is added to the former till the red precipitate of mercuric iodide is on the point of becoming permanent. This solution applied to the image converts the silver into double iodide of mercury and silver, which is very non-actinic in character; other similar methods may be adopted, all depending on the formation of double metallic compounds. By converting the silver image into iodide by the application of the iodine solution, and then flooding with sodium sulph-antimoniate (Na_2S,SbS_5) commonly known as Schlippe's salts, a scarlet deposit is produced of silver sulph-antimoniate in which 2 atoms of silver replace the 2 atoms of sodium, the iodine combining with the sodium. This method of intensification is due to Carey Lea, who described it in a paper which appeared in February 1865 in the American 'Journal of Photography.' Schlippe's salts are prepared by taking

Antimony bisulphide (finely powdered) .	18 parts
Dried sodium carbonate	12 parts
Caustic soda	13 parts
Sulphur	3½ parts

These are ground up into a fine paste with a little water, and transferred to a well-closed stopped bottle, completely

filled with water. After digestion and agitation for twenty-four hours, the clear liquid is filtered off, and allowed to evaporate spontaneously in a closed vessel over sulphuric acid, till lemon-coloured crystals of a regular tetrahedral shape are obtained. These are dissolved in water immediately before use, as the solution deposits an antimony compound when kept. The mother liquor may be employed for intensifying, but does not answer so well as the salt itself. The quality of the colour is dependent on the amount of silver converted into iodide or chloride.

When great density is required without gradation of shade, the following formula is efficient when preceded by a saturated solution of mercuric chloride.

The effect of this compound, as already pointed out, is to form a double chloride of silver and mercury, grey at first, but which subsequently becomes converted into a pure white deposit. When in this state, if

Ammonium sulphide . . .	50 c.c.
Water	1 litre

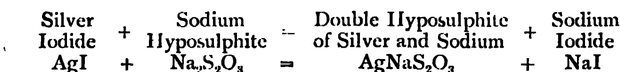
is applied, a double sulphide is formed of an intense black. Dilute ammonium hydrate may also be employed, as already stated, in place of the sulphide.

As regards the treatment of an image with copper bromide, this salt may be formed by dissolving 1 gramme of copper sulphate in 10 c.c. of water and adding an equivalent of potassium bromide to it. This solution is flowed over the plate, and after a whitening action on the film and thorough washing, a 20 per cent. solution of silver nitrate is applied.

Fixing the Image

As regards fixing the image, nothing need be said excepting that the solvent used must be incapable of readily attacking the metallic image, and such are the solutions of sodium hyposulphite and potassium cyanide. It will be useful here to point out the mode by which this solution is

effected. Supposing, for instance, the image be developed on the iodide of silver; we have on addition of sodium hyposulphite either



Silver Iodide	+	Sodium Hyposulphite	=	Double Hyposulphite of Silver and Sodium	+	Sodium Iodide
AgI	+	$Na_2S_2O_3$	=	$AgNaS_2O_3$	+	NaI

or



$$2AgI + 3Na_2S_2O_3 = Ag_2Na_4 3(S_2O_3) + 2NaI$$

The first silver hyposulphite is very soluble in water, whilst the last is very insoluble; we have, therefore, in using sodium hyposulphite, a danger of the formation of the insoluble compound—a danger not to be under-estimated in the matter of silver prints, when the elimination of the less soluble compound is a matter of great difficulty.

With potassium cyanide the danger does not exist, for though silver cyanide is formed, yet it is readily soluble in a small excess of the potassium compound.



Silver Iodide		Potassium Cyanide		Double Cyanide of Silver and Potassium		Potassium Iodide
AgI	+	$2KCN$	=	$AgCN \cdot KCN$	+	KI

Instead of AgI in the above equations, we may substitute nearly every silver compound—thus $AgNO_3$, $AgCl$, $AgBr$, $AgOSiO_2$. Potassium cyanide, however, has the drawback that it is excessively poisonous, and that the presence of acid causes it to evolve hydrocyanic acid, a gas the deadly effects of which it is unnecessary to comment on. Another drawback to its use is the danger that exists of its dissolving up the finely deposited metallic silver, of which the half-tones of the image is composed. If used in a sufficiently weak solution, however, the solvent action need not be feared. All traces of the hyposulphite and cyanides should be removed by thorough washing, otherwise the transparent parts of the image might discolour, or a disintegration of the film might take place through crystallisation.

The following solutions are those generally employed:

Sodium hyposulphite . . .	100 grammes
Water	500 c.c.

and,

Potassium cyanide	30 grammes
Water	500 c.c.

Varnishing the Film

A collodion film being excessively delicate and easily torn or scratched, photographers have adopted the plan of covering it with a transparent film of hard resin. This is effected by dissolving the resin in spirits, such as alcohol, and flowing it over the surface. In practice it will be found that, in order with safety to cover the film without dissolving or disintegrating it, the specific gravity of the methylated alcohol, with which for economy it is made, should be greater than that employed in the manufacture of the collodion. It may at first sight seem strange that alcohol should be capable of attacking the pyroxyline, but it must be remembered that undiluted methyl compounds are solvents of it, and, unless sufficient water be present in the varnish to check the tendency, a disintegration at least will take place. It must also be remembered that the rate at which the solvent evaporates will cause a difference in the transparency of the coating. If it be allowed to evaporate spontaneously, the alcohol evaporates first, and leaves the water behind, and, as anyone will find if he drop a little varnish into water, the resin at once separates in minute particles, which, when so united together, give a translucent deposit, caused by the reflections of the various surfaces. On the other hand, if heat be applied, and the water be caused to disappear as rapidly or nearly as rapidly as the alcohol, the resin will dry transparent, the heat being sufficient to cause the particles to be bound one to another, thus eliminating all chance of particular reflection.

The resin should be as colourless as possible, as even the thin coating given to a negative picture is often sufficient to cut off much of the actinic light if it be of a red or yellow tint. As an experiment, it is only necessary to dissolve red Australian gum in spirit or water, and apply it to a portion of a glass plate, when it will be found that sensitive chloride paper darkens much less rapidly where covered with it than where it is bare.

The constituents of most varnishes usually comprise amongst them lac and sandarac, but it is a matter of the greatest nicety to proportion them in such a manner that the film shall not split after exposure to any great variation in temperature. The cause of the contraction that takes place is not accounted for; it seems that some resins have a property of attracting moisture, and almost becoming hydrates. This might cause an expansion of the film, whilst a rise of temperature might cause contraction. The whole blame, however, must not be laid upon the varnish, as the collodion film, when not free to expand and contract as it likes, may often produce the same effect. The following varnishes have been found satisfactory:

Unbleached lac	65 grammes
Sandarac	65 grammes
Canada balsam	4 grammes
Oil of thyme or lavender	32 c.c.
Alcohol, ·830	500 c.c.

or,

Seed lac	120 grammes
Methylated spirit	1 litre

The lac is allowed to remain in contact with the solution for two or three days, with occasional shaking; after which the supernatant liquid is decanted off, and thinned down to proper fluidity.

For gelatine plates there is no better varnish than celloidin dissolved in amyl acetate. It is water-white, will bear very rough usage, and is waterproof. It is now a recognised article of commerce, and can be obtained from the dealers.

CHAPTER VIII

EFFECT OF THE SPECTRUM ON THE HALOID SALTS OF SILVER

It will be a useful record to make to give the sensitiveness of the different salts of silver to the action of the spectrum, and the following are the results of some researches[1] made by the writer and communicated to the Royal Society.

Silver Iodide

Visible Effect of the Spectrum on Silver Iodide.—If paper be soaked in a 10 per cent. solution of potassium iodide and dried, and then be floated on a 10 per cent. solution of silver nitrate and exposed whilst moist,[2] the spectrum will be impressed in five minutes, as given in No. 1, fig. 9, where it will be seen that the whole visible spectrum is impressed. Similar paper, if exposed to the spectrum coming through a weak solution of potassium chromate, exhibits after ten minutes a slight action in the least refrangible region. If, however, the paper be exposed for ten seconds to diffused light and then be exposed to the same spectrum as the last, the action is more intense than before, though the exposure be for only two minutes. From this we learn that part of the action of the spectrum in No. 1 is due to the action of diffused light. It next remained to trace the action on the different silver compounds existing in this paper, which was ordinary sized saxe paper. Paper was prepared as before, but washed in common water till nearly all excess of silver nitrate was eliminated, and it was then given a wash of potassium nitrite, an absorbent of iodine. Such paper was exposed to the spectrum, first, coming through chromate, second, unshaded. The print obtained is that shown in

[1] *Proceedings, Royal Society*, No. 217, 1887.

[2] The same action was observed where the paper was allowed to dry, but the darkening was less.

No. 2, fig. 9, by which it will be seen the same limits were reached as before, but that there is not that abrupt descent of sensitiveness near G; evidently some cause of the extreme sensitiveness near this point had been eliminated, and apparently that could only be the silver nitrate and the presence of the potassium nitrite. To test the matter further, paper was prepared in the same manner, but before applying the potassium nitrite it was soaked in common salt and water and washed. This would effectually remove all traces of silver nitrate, converting it into silver chloride. Exposure for five minutes to the spectrum gave the result shown in No. 3, in which it will be seen that whilst the most refrangible portion took a grey colour, the small portion below G became pink, the line of demarcation between the two being well defined. It now seemed probable that the pink part of the spectrum was due to the chloride and the grey to the iodide.

To further investigate the matter, the same paper without iodide was floated on silver nitrate and exposed to the spectrum, with the result given in No. 4, a very faint trace of action being visible where the paper was exposed for a quarter of an hour to the spectrum transmitted by the potassium chromate.

Iodised paper prepared as in the first experiment was well washed and simply exposed, with the result to be seen in No. 5. Finally, paper was prepared and washed, then immersed in a weak solution of potassium iodide, washed well and flooded with potassium nitrite, and the result is given in No. 6. No. 1 coincides with the observations made by Sir J. Herschel, on paper similarly prepared, in 1842, and described in the 'Phil. Trans.' for 1843, and he classes this spectrum as due to the silver iodide. It will be seen that the printed spectrum due to silver iodide is that given in No. 8, and that the tail extending to the least refrangible end is really due to the action of that region on the organic salt (and perhaps chloride) of silver present in the paper.

Further, it will be seen that the greater part of the darkening in No. 1 of that tail is due to the action of the different rays after or whilst diffused light has acted or is acting on that organic compound. Confirmatory experiments were made with pure silver iodide in collodion, with excess of silver nitrate, and also without such excess, with the result shown in No. 8.

Thus, then, we may say that the parts of the spectrum capable of direct action on silver iodide are shown in No. 6.

In these experiments different acid developers prove this, and proceed to give the same results as did the alkaline and organic iron developers.

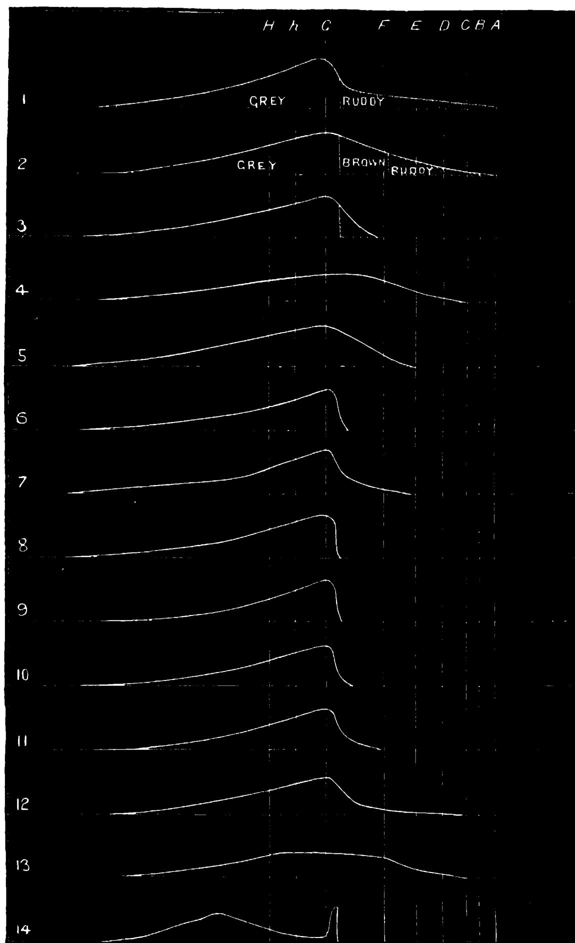
It may be necessary to point to the different materials employed.

Five grains of commercial cadmium iodide were dissolved in an ounce of collodion, and this was also used with a silver nitrate sensitising bath. The pyroxyline forming the collodion was carefully selected. Before taking into use it had been precipitated from solution by water, washed in alcohol, again precipitated, and washed and dried, and then redissolved in equal parts of pure ether and alcohol at the rate of 7 grs. to each ounce. Such a solution after prolonged exposure when impregnated with nitrate of silver gave no reduction of the salt.

The emulsions of silver iodide were made by dissolving 6 grs. of silver nitrate in alcohol, adding this to collodion, and gently adding the equivalent to 5 grs. of silver nitrate of the soluble iodide (dissolved in alcohol) to it. This formed a perfect emulsion of silver iodide in the presence of a slight excess of silver nitrate, and also of course of the soluble nitrates formed by the double decomposition of the above. The presence or absence of these soluble nitrates had no effect at all on the results, and may at once be dismissed from further consideration.

Gelatine emulsion was prepared in the same manner, keeping in mind, however, that in this case it was prepared

Fig. 9.



1. $AgI+AgNO_3$ on paper (*print*). 2. AgI on paper washed from excess of $AgNO_3$ and treated with KNO_2 (*print*). 3. AgI on paper washed from $AgNO_3$ soaked in NaCl, washed from excess and exposed with KNO_2 (*print*). 4. Paper

with an excess of soluble iodide instead of silver nitrate. It is well to remark that it is impossible to get a fine emulsion of silver iodide in collodion unless the plan indicated above be followed of first dissolving the silver nitrate in the collodion and then adding the iodide to that, in addition to which it is necessary that the silver nitrate be in excess or the emulsion becomes granular. With gelatine the emulsification is an easier matter, but in order to prevent spontaneous decomposition of the gelatine it is necessary that the soluble iodide be in excess. Emulsions of both kinds were 'washed' by the usual methods explained in chap. xix. In the case of the collodio-iodide of silver great care was taken that nothing but pure distilled water was employed.

It will be well to show here how it was we ascertained that nothing but pure iodide of silver exists in a film. The impurities to be met with are oxides, chlorides, and bromides. Now when an oxide of silver, or silver chloride or bromide is placed in a solution of potassium or other soluble iodide, the silver compound is at once decomposed, and silver iodide formed in its place. If, then, a film of iodide of silver in collodion (whether prepared from an emulsion or by the bath process) be washed from silver nitrate, and be then immersed in a weak solution of potassium iodide (it must not be strong or it will dissolve out the silver iodide from the film) or other soluble iodide, it may be seen that there will be nothing but silver iodide in the film, all impurities being decomposed. If the film be washed well with distilled water, and again immersed in the bath, or flooded over with some sensitiser, such as potassium nitrite,

floated on $AgNO_3$ (*print*). 5. AgI on paper washed from excess of $AgNO_3$, ruddy tint (*print*). 6. AgI on paper washed from excess of $AgNO_3$, treated with KI and KNO_2; or AgI in collodion (*print*). 7. AgI + $AgNO_3$ in albumen (*print*). 8. AgI prepared in bath treated with KI, washed, redipped in silver bath, developed with pyrogallic acid (*developed*). 9. AgI purified and exposed in presence of sensitiser, developed by acid or alkaline developer (*developed*). 10. AgI unpurified, treated and developed as above (*developed*). 11. AgI with trace of AgCl or AgBr, developed by acid or alkaline method (*developed*, long exposure). 12. AgI + $AgNO_3$ in albumenised collodion, or on paper washed, acid development (*developed*). 13. AgI + $AgNO_3$ in albumenised collodion, or on paper washed, ferrous citrate eveloper (*developed*). 14. AgI + $AgNO_3$ prolonged exposure (*developea*).

sodium sulphite, beer, pyrogallic acid, &c., it may be exposed with the certainty that only pure silver iodide is under examination. It is necessary to make these remarks, since the whole of the utility of the research depends on the use of the pure substance, the collodion being absolutely inert as regards the silver salt. The silver iodide emulsion made from the purified potassium iodide proved to contain nothing but the pure iodide, but that prepared with the cadmium and other iodides, as will be seen, proved untrustworthy as to purity.

One word also as to the neutral or alkaline developer employed. It has been customary to state that silver iodide is unamenable to alkaline development. This is, however, not the case. The ferrous oxalate and the ferrous citro-oxalate bring out a distinct image, as does pyrogallic acid and ammonia, when no restraining iodide is employed. In all dry plates prepared with the iodide and other silver haloids, the iodide is developable (though it gives a weak image compared with that due to other salts) by the alkaline or organic iron developer.

A plate was coated with cadmium iodised collodion, and placed in the bath for a couple of minutes, and exposed to the spectrum. The result is seen in No. 10. The development took place by the acid developer. Plates similarly prepared and washed and then similarly exposed also gave as results No. 10. When using ferrous oxalate, the cadmium emulsion also gave the same result. Plates coated with a film of the same collodion, washed, and then immersed in a weak solution of potassium iodide or cadmium iodide, again washed clean with distilled water, and finally treated with silver nitrate, beer, pyrogallic acid, potassium nitrite, when developed by the acid or other methods gave the results in No. 8. The purification of silver iodide by this treatment cut off the small tail on the least refrangible side of G, seen in No. 10. When the pure silver iodide prepared by the aid of the pure potassium

iodide was used, No. 9 resulted. A plate was next coated with collodion iodised with the pure potassium iodide, im mersed in the bath, washed, and then placed in a solution of common salt (1 gr. to 5 oz.), with the result that figures similar to No. 11 were obtained.

A plate similarly treated, except that potassium bromide was substituted for the common salt, also gave as a result No. 11. There was no marked difference whether the plate was developed by the acid developer or by the ferrous oxalate. It would be useless to describe the many other experiments which were made, all tending to prove that the true action of the spectrum on silver iodide in collodion is that given in No. 8. No deviation from it has been obtained, unless impurity in the pyroxyline or in the soluble iodide was proved to exist.

With gelatine emulsions of yellow silver iodide, when rendered sensitive by the use of potassium nitrite or silver nitrate, the same action was found to hold good, and the same may be said for plates prepared with albumen as a vehicle, when all silver was converted into iodide, and the sensitising was effected by potassium nitrite or some other similar sensitiser.

We next come to the iodide of silver when held *in situ* by paper. The same method of preparation was adopted as that given above for the printing experiments. When paper was exposed with the excess of silver nitrate, on acid development No. 12 was obtained. When developed by an organic ferrous developer, No. 13 was obtained; No. 10 was obtained when similar paper was washed and salted with common salt, and washed again, and then sensitised with potassium nitrite.

Nos. 12 and 13 are worthy of attention. It is seen in No. 12 that the iodide has much greater power of attracting freshly deposited silver than have the impurities present with it in the paper. On the other hand, No. 13 shows that the ferrous oxalate developer has more power of reducing the

impurity (or rather the reduction is better seen) than it has the iodide.

When silver iodide paper is prepared and washed, and treated with a weak solution of potassium iodide and re-sensitised by potassium nitrite, No. 8 is obtained.

No. 14 shows the action of the spectrum on pure iodide when the exposure is very prolonged. It appears as if the sensitiveness on the more refrangible side of G had diminished. This is not the case, however. The prolonged exposure causes a commencement of what is called a reversal of the image due to oxidation, which will be noticed further on, and the maximum effect has, therefore, apparently shifted to the least refrangible side of G, as shown. This is important, since phenomena which have been described and figured by other investigators can be shown to be caused by this reversing action.

What has been noted regarding the action of impurities in the silver iodide points to a method of ascertaining if an iodide or the iodine itself is pure. It is believed that the merest trace of impurity may be recognised by this method of spectrum analysis.

Silver Bromide

When paper is immersed in a 10 per cent. solution of potassium bromide, then dried and floated on a 10 per cent. solution of silver nitrate, and exposed to the action of the spectrum, the visible effect will be observed as shown in No. 15, fig. 10. It is needless to go into all the details which were described when silver iodide paper was under examination. The same causes exist for the shape of the curve as they do with the latter paper. It may be interesting to remark that the spectrum observed on paper which has been washed and treated with potassium bromide after sensitising is the same as that shown in No. 17, whilst when only washed and not treated with the soluble bromide it takes the form of No. 20. The reason of these differ-

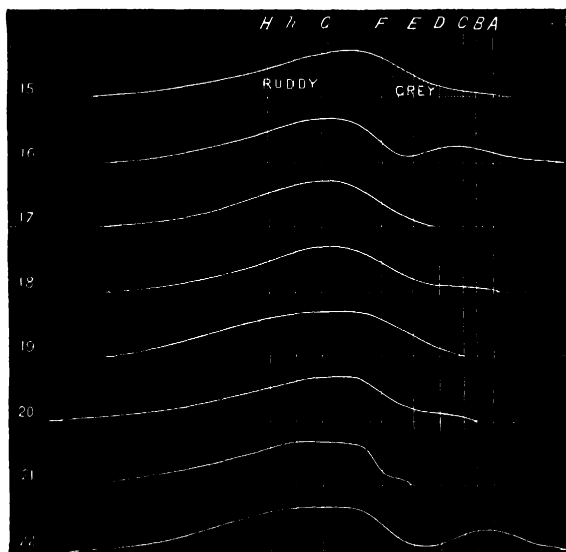
ences in shape of curve is apparent when it is remembered how the effects on silver iodide paper were traced to their source.

It must be noted that there are several molecular modifications of silver bromide. • The first is that form in which it exists in the paper and also in collodio-bromide emulsions when prepared in the ordinary way; also when prepared in collodion by the bath. This form transmits a yellow-orange tint when white light traverses it. Another form is one which the writer described in the Bakerian Lecture for 1880, viz. a form which transmits a blue-green tint; and a last form which transmits a grey tint, which is found in gelatine emulsions which have been boiled, or treated with ammonia in the manner which is common at the present day. These three varieties were examined both for the visible action of light and also for development. A plate was coated with the first emulsion named, with the result that the direct action of light gave No. 17. The blue-green transmitting form gave No. 16. This form is one which is sensitive to the infra-red rays of the spectrum on development, and it will be seen that the printing action also extended to that region. The printing action on the grey form (which was submitted to the spectrum in a film of gelatine) is shown in No. 18. On comparing these together, it will be seen that the maximum action commences between G and F (nearer F than G), and that the main difference in their impressed spectra lies in the tails on the least refrangible side. When the colour transmitted by these three forms is taken into account, these differences are to be expected. Whether the silver bromides were exposed with a slight excess of silver nitrate, or with a slight excess of soluble bromide, no difference in the spectra resulted.

We next come to spectra developed on the different preparations of silver bromide. No. 19 represents the action of the spectrum on silver bromide paper, prepared

as above, which has been washed. Whether development took place by acid developer or by ferrous citro-oxalate, no difference was observable. When the paper was washed and treated with potassium bromide and then exposed, we have as a result No. 21.

FIG. 10.



15. AgBr+AgNO$_3$ on paper (*print*). 16. Green AgBr in collodion with or without AgNO$_3$ (*print*). 17. Orange AgBr in collodion gelatine with or without AgNO$_3$ (*print*). 18. Grey AgBr in gelatine (*print*). 19. AgBr on paper washed from AgNO$_3$, developed with acid or ferrous citro-oxalate developer (*developed*). 20. Grey AgBr in gelatine, developed alkaline or ferrous oxalate (*developed*). 21. Orange AgBr in collodion or gelatine, developed alkaline ferrous oxalate or acid developer (*developed*). 22. Green AgBr in collodion, developed ferrous oxalate (*developed*).

When a plate is coated with collodion containing cadmium bromide, zinc bromide, or potassium bromide, and placed in a strong silver nitrate bath, and developed with either acid developer or with ferrous citro-oxalate, we get curves similar to No. 21. The same figure also represents

the action of the spectrum or collodio-bromide emulsions transmitting orange light by any kind of development. This applies equally whether the plate be exposed wet or dry, or whether exposed in the presence of silver nitrate or other inorganic sensitisers.

No. 20 shows the results obtained when using gelatine bromide plates with the silver bromide in the grey molecular state, whether exposed with an inorganic sensitiser, or without, and whether developed with an acid, alkaline, or organic iron developer.

No. 22 represents the action on the blue-green molecular form of silver bromide in collodion, when developed and exposed under similar circumstances to the preceding case.

It will be remarked that the direct visible action of the spectrum and the developed image coincide.

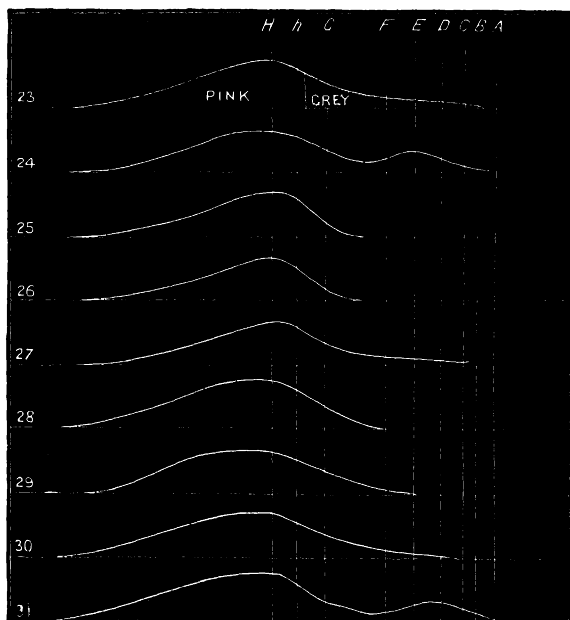
The effect of impurity in the bromide is not so marked as it is in the iodide. The presence of iodide except in minute quantities is rare; the haloid most frequently present as an impurity being the chloride. When the spectrum on the chloride is considered, it will be seen that such an impurity is hardly possible to be detected, as the spectra impressed on it are somewhat similar in general character to those on the bromide.

Silver Chloride

Paper was impregnated with a 10 per cent. solution of sodium chloride and sensitised on a 10 per cent. solution of silver nitrate. Paper thus prepared was exposed to the spectrum in a damp state, and also in a dry state, and the visible impression recorded. No. 23, fig. 11, shows the action. When the paper was exposed for twenty seconds to diffused light a different curve as shown in No. 24 was found; an approach to the same curve being also shown with very prolonged exposure without the preliminary action of light. This is probably due to the action of the diffused light in the prism. We have not here taken into

consideration the spectrum impressed on silver chloride visibly darkened by the light. This, as is well known, is impressed throughout the spectrum, and takes the approxi-

FIG. 11.



23. AgCl+$AgNO_3$ on paper (*print*). 24. AgCl+$AgNO_3$ on paper, slight preliminary exposure (*print*). 25. AgCl on paper washed from excess of $AgNO_3$ (*print*). 26. AgCl on paper washed and treated with NaCl and washed again, also collodion chloride of silver, also yellow form of AgCl in gelatine (*print*). 27. Grey form of AgCl in gelatine (*print*). 28. AgCl in collodion in presence of excess of $AgNO_3$ or NaCl developed; ferrous citrate, or acid development (*developed*). 29. Yellow form of AgCl in gelatine, acid, or ferrous citro-oxalate development (*developed*). 30. Grey form of AgCl in gelatine, acid, or ferrous citro-oxalate development (*developed*). 31. AgCl in collodion given a short preliminary exposure, acid, or ferrous citro-oxalate development (*developed*).

mate colour of the spectrum. This is true whatever vehicle is used to hold the silver chloride, and also whether exposed in the presence of an excess of silver

nitrate or other sensitiser, and also when organic compounds of silver are mixed with it.

Similar paper was washed, some was used in this state and other was afterwards treated with a solution of sodium chloride and again washed, leaving thus only a trace of an organic salt of silver in the fibre. The action of the spectrum on the simply washed paper is shown in No. 25. With a short preliminary exposure, traces of an impression between F and C were obtained, tending to show that the preliminary action in No. 24 was effective on the chloride besides on the organic compound of silver. No. 26 gives the action of the spectrum in the chloride which had all traces of silver nitrate removed by the wash of sodium chloride.

To obtain an emulsion of silver chloride in collodion, 20 grs. of calcium chloride were dissolved in 1 oz. of collodion, and 1 gr. more, or 1 gr. less, according as excess or defect of silver nitrate was required, then the equivalent of silver nitrate was dissolved in another ounce of collodion; the former solution was poured in the latter, shaking at intervals, till a perfect emulsion was obtained. In some cases the emulsion was washed in the ordinary way known to photographers, and in others used when made as above, and the films washed or exposed in their natural state. In no case did any difference in the resulting impression of the spectrum appear. We may also state that other chlorides were tried, and there is no apparent difference from those obtained where sodium chloride was employed. No. 26 also gives the action of the spectrum on such emulsion, there being no apparent difference between the washed emulsion or the emulsion exposed with an excess of silver nitrate, or with an excess of the soluble chloride, unless it be one of general sensitiveness. In other words, the spectrum seemed to act on the silver chloride in one and the same manner. No. 27 shows the printing action on the chloride when enveloped in gelatine. The emulsion was

formed in the usual manner habitual amongst photographers, each ounce of emulsion containing about 25 grs. of converted silver nitrate. No. 27 has reference to this emulsion after it was heated to its boiling point for half an hour, and when treated with ammonia; when used unboiled it took an impression similar to No. 26.

When these same preparations of the chloride in gelatine are exposed for a short time to the spectrum and developed with ferrous citro-oxalate developer, or with gallic acid and silver, we get Nos. 29 and 30, the former expressing the result of the unboiled emulsion which transmits yellow-orange light, and the latter number that on the boiled emulsion which transmits blue-grey light.

Silver chloride in collodion by whatever means prepared, and whether exposed with an excess of silver nitrate, or an excess of soluble chloride, gave No. 28, the former being the result of exposure ten times longer than that shown by the latter. The mode of development had no effect on the spectrum developed.

The washed paper gave on development the same result as that shown for the direct action of light, viz. No. 27. The mode of development had no effect on the result.

The washed paper subsequently treated with a solution of sodium chloride and again washed, when exposed to the spectrum gave on development with either gallic acid, and silver nitrate, or with ferrous citro-oxalate, the same figure as that obtained by the direct action of light, viz. No. 26.

When a brief preliminary exposure to white light was given to either the paper or the different emulsions, No. 31 was obtained on development. On looking at Nos. 23 to 31 it will be seen that invariably the maximum intensity is reached between H and *h*. According to many authors the maximum is near G, whilst according to others it is in the ultra-violet. We carried out about 200 experiments on the chloride with sunlight and with the electric light, and in

no case has it been found possible to alter the position of the maximum.

Methods of obtaining Mixtures of Silver Iodide and Bromide, Silver Iodide and Chloride, &c.

To test mixtures of the iodide and bromide, paper was prepared by immersing it in a solution of potassium iodide and potassium bromide, the proportion of each being so arranged that there should be definite proportions between them, supposing that each salt was entirely decomposed by the silver nitrate. Unfortunately this is never absolutely the case, and hence the results obtained with the paper must be received with some caution. Chemists know that silver bromide or silver chloride cannot exist in the presence of a soluble iodide, nor can silver chloride in presence of a soluble bromide. Hence when we have an iodide and bromide impregnating paper, the silver iodide will first be formed, and then the bromide; or, again, with iodide and chloride, the silver iodide will first be formed and then the chloride; and finally, with bromide and chloride, the bromide will first be formed and then the chloride.

It was necessary to make these remarks, as a right conception of the results might not be taken on casually looking at them.

The same remarks apply with equal force when a sensitive film of the double salts is prepared by the ordinary silver bath, when very short immersion is given to the plate. The only true way of obtaining definite results seems to be by means of separate emulsions, in which a definite amount of soluble chloride, bromide, or iodide is fully converted into silver chloride, bromide, or iodide, and then to mix these emulsions, after proper washing, in the required proportions. It was in this manner that the emulsions which will be discussed presently were prepared.

We would here call attention to a somewhat remarkable

behaviour of silver iodide. It is well known that if silver iodide be prepared with an excess of soluble iodide, it is totally insensitive to light. Thus if we prepare (say) an emulsion in collodion with an excess of iodide, and wash it thoroughly in the usual manner, and after redissolving the pellicle resulting from the washing operations, expose it in the camera, no amount of development will bring out an image. If, however, to such an emulsion but a drop of a bromide or chloride emulsion be added sensitiveness will appear. This seems to be due to the last trace of soluble iodide being converted into silver iodide.

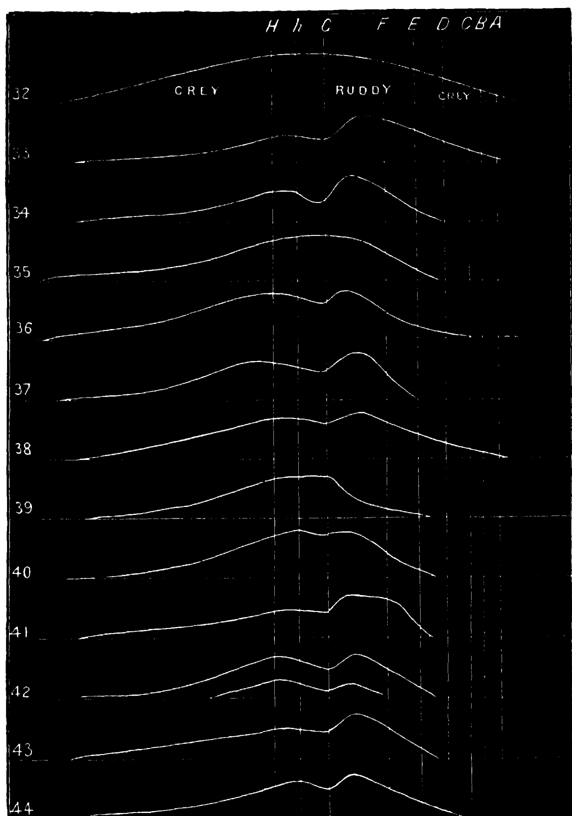
Mixtures of Silver Iodide and Bromide

Equal Equivalent Proportions of Iodide and Bromide.—Paper was soaked in a solution of equivalent proportions of soluble iodides and bromides, and, after drying, was sensitised on a 10 per cent. solution of silver nitrate for such a time that the back of the paper became thoroughly damp. The silver nitrate solution was acidified in order to prevent the formation of any subsalts.

A strip of such paper was exposed to the spectrum whilst moist, and the printing action noted. The result is given in No. 32, fig. 12. Similar paper was washed and treated with potassium nitrite, and exposed whilst moist; the effect of the action of the spectrum is seen in the same figure.

Paper was next washed, and portions were treated with a solution of potassium bromide, and again washed. Strips of these two specimens were dried and exposed to the spectrum, and in both cases the printing action is seen in No. 33. Similar papers, in a moist state, were also exposed without any deviation of the result. Again, paper which had been prepared as above was allowed to dry with the excess of silver nitrate on it, and exposed, and No. 33 again approximately resulted; as also it did when the washed paper treated with potassium nitrite was dried.

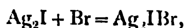
FIG. 12.



32. AgI + AgBr + $AgNO_3$ on paper, moist (*print*). 33. AgI + AgBr, washed from $AgNO_3$ (*print*). 34. Ditto, ditto, developed ferrous citro-oxalate (*developed*). 35. AgI + AgBr + $AgNO_3$, wet plate, developed, acid, or alkaline developer (*developed*). 36. AgI + AgBr in gelatine, developed ferrous oxalate (*developed*). 37. AgBr + AgI in collodion, acid or alkaline developer (*developed*). 38. 3AgI + AgBr on paper (*print*). 39. 3AgI + AgBr on paper developed gallic acid (*developed*). 40. Ditto, developed ferrous citrate (*developed*). 41. 3AgI + AgBr + $AgNO_3$ collodion, wet plate, acid, or alkaline developer (*developed*). 42. 3AgI + AgBr in gelatine, alkaline, or ferrous oxalate developer (*developed*, long and short exposure shown). 43. AgI + 3AgBr on paper or in collodion, ferrous citro-oxalate developer (*developed*). 44. AgI + 3AgBr in gelatine ferrous oxalate developer (*developed*).

The difference between curves 32 and 33 is very remarkable, and at first sight might not seem to admit of explanation. A study of the experiments described, however, affords a clue to the apparent incongruity of the results. According to text-books on chemistry, bromine will displace iodine in combination, whilst iodide displaces bromide. Later researches seem to modify the first statement to a certain extent. Bromine will only displace a definite proportion of iodine when it is in excess; but for our purpose we may take the text-book statement as practically correct. When the paper was exposed wet with either silver nitrate or potassium nitrite (other halogen absorbents gave the same result) the iodine and bromine liberated by the action of light would be at once absorbed by them; in the one case silver iodide (or bromide) and silver iodate (or bromate) being formed, and in the other potassium iodide (or bromide); so that each of the two kinds of sensitive salt would have its full action. When the paper was washed and exposed in a dry state the result would be different, and the question would arise, what would become of the iodine and bromine liberated by light?

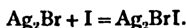
If silver iodide be exposed to light and treated with a trace of bromine, the subiodide combines with the bromine, and all trace of the action of light is destroyed. Thus when the mixture of iodide and bromide is exposed to light, both iodine and bromine being liberated, the bromine will at once combine with the subiodide and destroy it. Thus,



$$Ag_2I + Br = Ag_2IBr,$$

the only factor remaining being the sub-bromide, which is developable. Now it may be said that the iodine liberated should also destroy the subsalts; but it is a matter of fact that, in the presence of light, it has no power of destroying the subiodide, since it is immediately again shaken off from

the molecule.[1] Iodine can destroy the sub-bromide molecule, and form a new saturated molecule ; thus,



$$Ag_2Br + I = Ag_2BrI.$$

Whether the two molecules Ag_2BrI and Ag_2IBr have the same value is a moot point, but the evidence tends to show that such is the case. If the equivalents of bromide and iodide were equal, that is, if the bromide and iodide of silver were equally distributed, supposing both the above actions took place, the locality of the spectrum in which the iodide and bromide are equally sensitive should show an almost entire destruction of a developable image, and also of a printed image.

This locality is doubtless about G, and when we come to analyse the curve No. 33 we see that there is very small effect about G, whilst there is an increased effect between G and F. Now, to test the matter further, paper prepared with washed silver bromide was exposed to light till it darkened thoroughly, and such paper was treated with a very dilute solution of iodine, and then exposed in the spectrum, with the result given in No. 55, in which it will be seen that the new molecule is more sensitive to the green between G and F than above G ; in fact, we have very little action comparatively at G and above it. In this case we have then a paper prepared in which there is an absolute imitation of the action that takes place in the mixed iodide and bromide. It cannot be said that by this treatment we have $Ag_2I_2 + Ag_2Br_2$, since the molecule formed by light is Ag_2Br, and the addition of the iodine is simply to form Ag_2BrI, which is very different from a simple mixture. This experiment then seems to show that this new molecule is more sensitive to the blue-green than it is to the violet. The question now arises as to how, when the original paper is

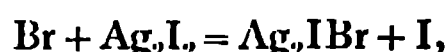
[1] It must be noted that the iodide is much less sensitive to light when no absorbent of iodine is present. This is fully accounted for by the immediate recombination of, at all events, a portion of the iodine liberated with the subiodide molecule.

exposed to the spectrum, we have not only a fall of sensitiveness at G and beyond it, but also a greater sensitiveness in the green. Now, silver iodide, as has already been shown, is not in the least sensitive to beyond a very small region below G; therefore, in the green the only component of the mixture of bromide and iodide that can be acted upon is the bromide. As we see when bromide is acted upon one atom of bromine is liberated from the molecule; thus,



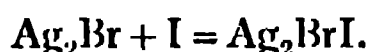
$$Ag_2Br_2 = Ag_2Br + Br.$$

The liberated atom of bromine immediately attacks the molecule of iodide in its immediate neighbourhood and forms a new bromo-iodide molecule liberating iodine. Thus,



$$Br + Ag_2I_2 = Ag_2IBr + I,$$

and the iodine either escapes or else forms the molecule Ag_2BrI; thus,



$$Ag_2Br + I = Ag_2BrI.$$

Here then it is probable that we have a new saturated molecule formed by the action of light, which on formation is susceptible of being acted on by light in its turn. Whether iodine or bromine is liberated from this new molecule we are not at present prepared to state, but it is our belief that it is the iodine, since density in development by the alkaline method is readily obtained when experimenting with it.

To sum up, the difference in shape between curves 32 and 33 seems to depend on the destruction of the sub-iodide when formed, and its conversion into a new molecule, which is sensitive to the blue-green, the same new molecule being formed by the liberation of the bromine from the molecule of silver bromide when the sub-bromide is formed. In the case of the paper which is dried in the presence of silver nitrate and potassium nitrite the same result occurs. Bromine and iodine attack these salts when in a crystalline state with difficulty, and hence will in preference form the new molecules as before.

No. 34 shows the curve of washed paper when developed with ferrous citro-oxalate, and nearly the same result is seen when the development proceeds by acid development, the difference being that the dip in the curve between *h* and G is less pronounced. To illustrate this further, in No. 35 we have the case of a collodion film containing equal parts of silver iodide and silver bromide and an excess of silver nitrate, the latter salt absorbing both the iodine and bromine liberated. In No. 37 we have the results obtained from the same film, but thoroughly washed from all excess of silver nitrate. Whether the plates be developed by acid, alkaline, or an organic ferrous salt, the curves remain in all essential particulars the same. In No. 36 we have the curve resulting from the same mixture (equal equivalent proportions) held in gelatine when developed by ferrous oxalate or alkaline developer. At first sight it might be said that this action is really due to the 'reversing action' of light. That this is not the case is shown by an exceedingly short exposure; in fact, when very quick exposure was given, the curve started at *h* and reached a maximum, as shown in No. 37. These results are excessively interesting and important. There is a figure showing something somewhat similar in Vogel's 'Lehrbuch der Photographie,' Berlin, 1878, but there is no explanation of the cause, nor has it been noticed by any other previous observer, as far as we are aware.

Three Equivalents of Iodide to One of Bromide.—When we take three equivalents of silver iodide to one of bromide the curves are somewhat modified. When washed paper prepared with the above proportions is allowed to print in the spectrum, we have the curve shown in No. 38. When exposed damp in the presence of silver nitrate or other inorganic sensitiser, we have almost a facsimile of the curve in No. 32.

Washed paper developed with acid developer shows that the proportion of iodide is so large in comparison to the bromide that the subiodide is not all destroyed, and

we get the maximum corresponding with the maximum of pure silver iodide, No. 39. The same paper developed with ferrous citrate shows a slight dip near G, No. 40. The difference in 39 and 40 is seemingly due to the fact that silver iodide has more attractive power for precipitating metallic silver than has the bromide (a fact which is well known) and that the bromide is more amenable to reduction than is the iodide.

No. 41 is well worthy of attention. It is the result of the exposure of a plate to the spectrum. It was prepared in the silver nitrate bath and exposed in the presence of free silver nitrate. Taking No. 41 alone, it might be supposed that we had a similar case to that which we have recently considered, since we find an extraordinarily (apparent) greater sensitiveness in the green than in the violet, and yet we have the image formed in the presence of an excess of silver nitrate, which would be against the theory promulgated. A short exposure, however, clears up the discrepancy: the maximum is found to be at G, and in this case the dip in the curve of No. 41 is caused by the reversing action alluded to.

No. 42 gives the curve obtained by the above mixture of three parts of iodide to one of bromide; when emulsified in gelatine the bottom curve shows a short exposure.

One Part of Iodide and Three of Bromide.—We now come to a mixture of one part of silver iodide to three of bromide. The printed spectra are not described since they correspond nearly with Nos. 32 and 33.

If we compare the curves in Nos. 43 and 41 we see a strange similarity between them, but if we take into consideration the curve due to a short exposure, it will be found that the dips about G are due to two different causes; the dip near G is caused by the formation of the new molecule. No. 43 is also the curve shown by paper prepared with the above equivalents of iodide and bromide, and also of the same in collodion when developed by an organic

ferrous salt. When developed by acid development, the curve in the more refrangible region is a little more pronounced in character.

No. 44 shows the same equivalents emulsified in gelatine and developed by ferrous oxalate.

The different equivalent proportions of bromide to iodide, it will be noticed, show themselves in the curves more particularly when a comparison is made between Nos. 36, 42, and 44.

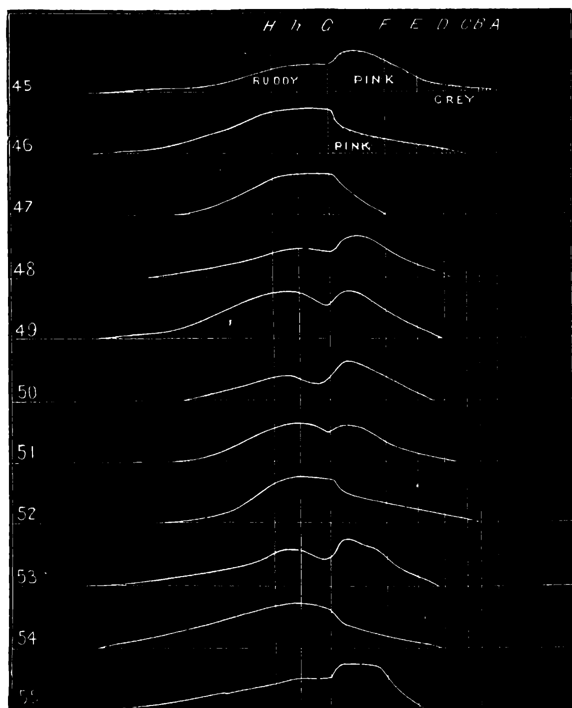
Mixture of Iodide and Chloride

Three Equivalents of Iodide to One of Chloride.—When paper is prepared with three equivalents of silver iodide to one of chloride and washed and dried, or if exposed in the presence of dried silver nitrate or dried potassium nitrite, we have the curve shown in No. 45, fig. 13. If, on the other hand, we have the same paper exposed moist, with silver nitrate or potassium nitrite, we have the curve shown in No. 46. The reasoning applied to the mixture of iodide and bromide applies with equal force here, the results being modified for the shift of maximum of the chloride which lies about ½ H*h*. In No. 45 the most refrangible part of the spectrum as far as G is ruddy, between G and F a pink colour, and beyond that grey. This difference in colour indicates (as it does in all other photographed spectra where different colours are impressed or developed) a difference of compound acted upon. According to our theory the molecule acted on beyond G in the violet and ultra-violet would be $Ag_2I_2 + AgICl$, and between G and E $Ag_2ICl + Ag_2Cl_2$ alone. The grey here is probably due to the organic silver compound formed in the paper.

No. 47 shows the same equivalents if contained in paper or collodion, and when exposed to light in the presence of moist silver nitrate or other inorganic sensitiser and developed by acid or ferrous citro-oxalate developer, the slight modification due to the former developer noted above

still holding good. No. 48 shows the same paper or collodion emulsion washed and developed with ferrous citro-oxalate. No. 49 shows the same when emulsified in gelatine and developed with the same ferrous developer.

FIG. 13.



45. $3AgI+AgCl+AgNO_3$ on paper, or ditto washed, both dry (*print*). 46. $AgI+AgCl+AgNO_3$ wet, or $3AgI+AgCl+KNO_3$ wet (*print*). 47. $3AGI+AgCl+AgNO_3$ or $3AgI+AgCl+KNO_3$ on paper, developed with gallic acid or ferrous citro-oxalate (*developed*). 48. Washed $3AgI+AgCl$ on paper, ferrous citro-oxalate developer (*developed*). 49. $3AgI+AgCl$ in gelatine, developed ferrous oxalate (*developed*). 50. $AgI+AgCl$ in gelatine developed ferrous oxalate (*developed*). 51. $AgI+3AgCl$ paper, washed (*print*). 52. $AgI+3AgCl+AgNO_3$ wet (*print*). 53. $AgI+3AgCl$ in gelatine, or on paper, developed with ferrous citro-oxalate or acid developer (*developed*). 54. $AgI+3AgCl+AgNO_3$, acid developer (*developed*). 55. AgBr exposed to light treated with I exposed to spectrum (*print and also developed*)

There is a difference in the curves obtained with collodion and gelatine, but not more than is explainable by the fact that the former is essentially porous and the latter almost continuous.

One Equivalent of Iodide to Three of Chloride.—When three equivalents of silver chloride are taken with one of iodide, we have, on printing a washed paper, the curve shown in No. 51; exposing the same paper moist in the presence of silver nitrate we have No. 52; the reasoning given when the mixture of bromide and iodide was under consideration holds good. Nos. 53 and 54 show the same equivalents of sensitive salts held in paper, the former showing the action of development on washed salts and the latter on the same exposed in the presence of moist silver nitrate.

No. 50 shows the effect of the spectrum on *equal* proportions of the iodide and chloride when emulsified in gelatine.

Paper and also collodion films containing silver chloride were blackened in the light and treated with a solution of iodine till the darkening was obliterated, washed, and then exposed, with or without sensitisers; we had nearly the same results on printing and on development as shown in No. 55, hence the curve is not repeated. (The same applies to darkened bromide treated with iodine, exposed to the spectrum and developed.) This appears to be a confirmation of the view already propounded regarding the formation of a new molecule, in the case of the chloride and iodide the new molecule taking the form of Ag_2ClI, as already indicated.

From these results we may observe that to obtain a compound sensitive to the green a mixture of iodide and bromide, or iodide and chloride, should be employed, the former in preference to the latter, since it is more sensitive. The same sensitiveness to daylight with the former in gelatine plates can be obtained as when using pure bromide alone, the sensitiveness being preserved by a shift of the maximum to the green.

Mixtures of Silver Chloride and Bromide

There is nothing special calling for remark in a mixture of these two sensitive salts. The printed spectrum and the developed spectrum seem to be a combination of the spectra impressed on each individually, a slight prolongation towards the least refrangible end taking place.

Mixture of Silver Iodide, Bromide, and Chloride

When these three salts are combined together we have spectra which are very similar to the spectra produced on iodide and chloride, or iodide and bromide, with a prolongation towards the red.

The writer, in a paper in the 'Proceedings of the Royal Society,' vol. xlvi., 1890, further confirmed the results which he had previously obtained, and, instead of an eye-estimation of the density, was able to make accurate measurements by which the comparative photographic images of different parts of the spectrum were deduced. It would be inadvisable to attempt to make an abstract of the paper, as it would require nearly the whole to be reproduced, and the reader is consequently referred to the original should he wish for further information.

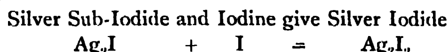
CHAPTER IX

ON THE APPARENT DESTRUCTION OF THE ACTION OF LIGHT ON THE PHOTOGRAPHIC PLATE

THERE is a phenomenon which we may now treat of, since the last chapter has described the ordinary action of the spectrum on the sensitive image. Several years ago[1] the writer made experiments on the causes of the apparent destruction of the photographic image, and

[1] *Philosophical Magazine*, June 1878.

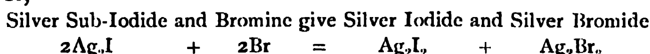
later on[1] showed how these causes explained the phenomenon of solarisation, or reversal of the photographic image. The image on the daguerreotype plate was long known to be destroyed by the action of the vapour of iodine, bromine, or chlorine. In fact, it was no uncommon thing in early days for an operator to resensitise a daguerreotype plate after exposure and before development by the means of one of these agents, the first image being totally destroyed. The action in this case is very simple. We have,



Silver Sub-Iodide and Iodine give Silver Iodide

$$Ag_2I + I = Ag_2I_2$$

or,

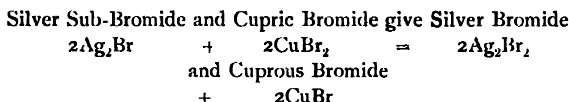


Silver Sub-Iodide and Bromine give Silver Iodide and Silver Bromide

$$2Ag_2I + 2Br = Ag_2I_2 + Ag_2Br_2$$

There are, however, other agents which the writer found destroyed the photographic image. It was found that all the mineral acids, and bromides and chlorides of certain dyad metals (such as cupric bromide and chloride) were equally effective, and that substances which readily parted with oxygen also destroyed the image.

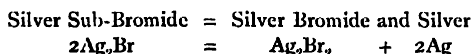
The chemical equations relating to the dyad bromides and chlorides can be well expressed thus:



Silver Sub-Bromide and Cupric Bromide give Silver Bromide and Cuprous Bromide

$$2Ag_2Br + 2CuBr_2 = 2Ag_2Br_2 + 2CuBr$$

With the mineral acids the chemical reaction is not so easy to explain. The effect is probably due to the conversion of the sub-bromide of silver into bromide by the abstraction of one atom of silver. Thus,



Silver Sub-Bromide = Silver Bromide and Silver

$$2Ag_2Br = Ag_2Br_2 + 2Ag$$

The atom of metallic silver is here supposed to be taken up by the acid.

[1] *Philosophical Magazine*, September 1880.

If a sensitive film of silver bromide in a collodion emulsion be placed after exposure in solutions of potassium bichromate, potassium permanganate, hydroxyl, &c., it is found that the action of light on a plate is also destroyed.

Experiments showed that this was due to the oxidation of the silver sub-bromide. This silver salt is unsaturated, and besides, metallic silver is capable of attracting other bodies, of which oxygen is one. When it has combined with it, unless such oxygen can be removed, the image becomes undevelopable, as there is no nucleus on which the metallic silver precipitated by the act of development can be deposited. Ozone has the same effect as the liquid solutions.

If a plate which has been exposed and subjected to the action of these oxidising agents be treated with nascent hydrogen, the image becomes developable, showing that when the oxygen has been removed the subsalt returns to its former activity.

These preliminary experiments led the writer to investigate the action of light on films which had been exposed to white light, and again exposed in solutions of many of these destructive agents in the presence of white light and of the spectrum, and also when exposed in presence of the alkaline haloids under similar conditions. The question to be solved was whether the action of light aided this destruction, and whether it applied also to the visible image.

Sir John Herschel has noted in the 'Philosophical Transactions' for 1840 that if paper be prepared with 1st, acetate of lead; 2nd, potassium iodide; 3rd, nitrate of silver, and be then darkened in the sun, and again be washed over with potassium iodide, on re-exposure to the sun the paper lightens again.

The experiment may be tried in a variety of ways. The simplest, perhaps, is to salt ordinary unglazed paper with a 10 per cent. solution of common salt, and when dry to float on a solution of silver nitrate of about the same strength, and then to dry and expose it to the daylight to blacken.

When the blackening is produced, if the paper be slightly washed and then be treated with a 5 per cent. solution of potassium iodide (slightly acidified with nitric acid) in the dark, and while still damp be exposed *beneath a negative* to the light, it will be found that those portions beneath the transparent portions will rapidly bleach, and we shall have a *negative image* instead of a positive, but reversed as regards right and left.

The same experiment may be repeated, substituting potassium bromide for the iodide, and the same results will be obtained. It may be asked if any metallic iodide or bromide will be effective; and to this an affirmative answer may be given; but the use of acid is not necessary in all cases. Those metals which form two iodides or bromides must be used extremely dilute, or the bleaching will take place in the dark—that is, supposing the highest type of bromide or iodide be employed. Thus a strong solution of zinc iodide may be used and acidified, whilst a very dilute solution of ferric iodide must be used.

Here then we have a proof that the visible image can be destroyed by the action of light. In this case the destruction is due to the liberation of the halogen from the metal or alkali by the action of light.

In the invisible but developable image the action is the same.

The following remarks are from the paper by the writer in the 'Philosophical Magazine':

If a plate be prepared with silver iodide by the ordinary wet process, be briefly exposed to light, and after washing be treated with a solution of potassium iodide and then be exposed to an image in the camera, after dipping in the silver-bath and developing, a positive image is obtained. It matters not whether the potassium iodide be alkaline, neutral, or acid, the same effect will be noted; also that there is no difference if, after treatment with the potassium iodide, the plate be washed or not, the reversal of the image

will still be shown. In this case the iodine is liberated as before, but the action is increased by the access of oxygen from the air ; in fact, it is a mixture of effects.

If potassium bromide or any simple bromide be substituted for the iodide, the same result obtains. Silver iodide, if prepared with an excess of soluble iodide, or if, after preparation with excess of silver, it be treated with a soluble bromide, is insensitive to light ; and the explanation of this perhaps may be found in the fact already stated.

It has been usually held that a soluble iodide, such as potassium, can destroy an invisible impression made by radiation ; but this is not so in the case of monad metals, if it be treated with the iodide in the dark. If, however, any iodide of a dyad, such as cupric or ferric iodide, be employed, which readily liberates an equivalent of iodine, the destruction is accomplished in the dark. The least favourable iodides for such destruction are the monads.

If a plate prepared with silver iodide have a preliminary exposure given it, and then be exposed *for a considerable time* to the image formed in the camera, a reversal of the image will take place as before. If, however, such a plate, after washing, be treated with an aqueous solution of pyrogallic acid, potassium nitrite, or any other deoxidising agent, such reversal of the image will not be obtained ; nor will it if it be exposed in a cell containing such a substance as benzene, or if exposed in dry hydrogen. From this we learn that, to obtain reversal, oxygen must be present in some form or another, and that, if a substance readily taking up oxygen be in contact with the silver-salt, a reversal cannot be readily obtained.

An interesting corroboration of the above statement is to be found in the exposure of an already exposed plate in a cell containing a dilute solution of permanganate of potash, bichromate of potash, or hydroxyl, when it will be found that the reversal takes place with the greatest facility.

The same reversals may also be obtained by using any of the mineral acids in a diluted form.[1]

The above experiments show, then, that a reversal may be obtained by the presence of the iodides or bromides (and in a more feeble manner, by that of the chlorides), and also by oxidising agents and mineral acids; whilst the presence of a deoxidising agent, or the exposure of the plate in a medium free from oxygen, prevents the occurrence of the phenomenon.

With the bromide of silver we have rather different phases of the phenomenon to consider. The development can be carried out with the alkaline or the ferrous oxalate developer, a mode which is more easy to carry out than the development by precipitation of metallic silver from an aqueous solution of silver nitrate. For experimental purposes, films containing silver bromide may be of collodion or of gelatine; but the behaviour of the silver-salt in the two vehicles is somewhat different, and has to be considered separately. Collodion is, or should be, a strictly neutral substance; that is, it is merely a medium in the pores of which the silver-salt is entangled and kept in position, and has no effect on the progress of development or on the action of light, beyond that which may be due to its physical qualities, its chemical constitution remaining unchanged.

The microscope tells us that a collodion film is essentially porous, and free access of the atmosphere to the silver is thus obtained. Gelatine, on the other hand, is a substance readily acted upon by oxidising agents and by the halogens; and consequently it may have an effect on the progress of development and on the action of light, its chemical constitution becoming altered. It is a homogeneous film, and not porous in the ordinary sense of the

[1] It must, however, be remembered that the solutions must be very dilute, or the whole effect of the preliminary exposure will be destroyed, since these oxidising agents are active in the dark, but act more readily in the light.

word, and is a protective agency against the atmosphere to those silver-salts which may be embedded in it.

If a film containing silver bromide, whether in gelatine or collodion, have a preliminary exposure given to it, and then be treated with a soluble bromide of an alkali, such as of potassium, and be again exposed to light in the camera, it will be found that there is not such a rapid reversal of the image as with the iodide, but that longer exposure is required to effect it, the reason being that bromide of silver prepared with a large excess of soluble bromide is still sensitive to light. If, therefore, the light decomposes the soluble bromide on the plate, liberating enough bromine to form fresh bromide of silver with the sub-bromide formed by the preliminary exposure, that freshly formed bromide, being sensitive to light, is again reduced to the sub-bromide state by the same rays which formed it. It will be evident, however, that reversal should take place more rapidly with the soluble bromide present than without it; and such is the case.

It is useless to treat a silver bromide film with a soluble iodide, since silver iodide is immediately formed, and the reactions that take place are similar to those already described.

If bromide of silver *in collodion* be exposed to the camera without the presence of any other substance, a reversal takes place. Roughly speaking, the reversal takes some sixty times more exposure to the light than is requisite to produce the maximum ordinary effect. To trace the cause of this reversal it is only necessary to treat the film with a 5 per cent. solution of potassium nitrite, when it will be found that the reversal does not take place. The same holds true when the film is treated with any deoxidising solution, or if the plate be immersed in benzene or hydrogen. The cause, then, of the reversal in this case is evidently an oxidation; and this may be further verified by treating the film, after a preliminary exposure, with bichromate of potash, hydroxyl, &c.; it will then be found that the reversal

takes place much more rapidly than when these oxidising agents were absent. The same may be said of the mineral acids.

If silver bromide be held in a gelatine film, the action of light is somewhat different. If the plate be exposed in the camera for a short time, say a few seconds, the image develops in the usual manner and we have a negative image; if it be prolonged to, say, a minute, the image is reversed on development; a further exposure causes a negative image to be produced, whilst one much more prolonged causes a positive image again to be formed on development. Here are four distinct phenomena[1] which need explanation. To solve the problem offered, plates should be exposed when saturated with a solution of potassium nitrite as before, when it will be found that the phenomena are absent, a reversal being almost impossible to obtain unless the length of exposure be such as to thoroughly oxidise the nitrite at the expense of gelatine. For ordinary purposes it may be said that a reversal is non-existent under these conditions.

If a plate be exposed in benzene, however (a liquid which does not permeate through gelatine), the phenomena are still existent. If a plate be exposed to such an extent that there is a marked image apparent before development, and be then immersed in water, it will be found that where the image appears the gelatine refuses to swell to the same extent that it does when the light has not acted. Taking these two experiments together, it is evident that the gelatine has played some part with the silver bromide. It may therefore be presumed that the last three phenomena are due, the 1st to the oxidation of the surface-particles of the bromide and a consequent change in colour, the 2nd to the change in colour of these particles permitting the coloured rays to which it is sensitive to strike a deeper layer, and the 3rd to the oxidation of this layer at the expense of the

[1] Mr. C. Bennett described these phenomena in the *British Journal of Photography* in 1878.

gelatine. The 3rd and 4th phenomena are so unimportant that they are scarcely worth investigating. The presence of organic matter is evidently necessary for their appearance; at least the writer has never been able to obtain them with collodion films not containing a preservative.

As before, the experiment of saturating one of these gelatine films with bichromate of potash shows that the reversing action is very much increased by the presence of the oxidising agent.

Having treated of these reversals of the image in a general way, it now remains to show which radiations are effective in producing them. For testing this, spectrum photography was resorted to, a special dark slide having been constructed capable of holding a cell which would contain the plate, together with the liquid, gas, or vapour whose action it might be desired to test. Three flint-glass prisms were used, and the lens of the camera had an equivalent focus of about 2 feet, the collimating lens being of the same focus. The time of exposure was, as a rule, three minutes to the sunlight or to that of the electric arc, care being taken in the latter case that an image of the positive pole fell on the slit so as to give a continuous spectrum. The action of potassium iodide on silver iodide will first be described.

A plate was exposed after being sensitised, and after washing was immersed in a cell containing a 1 per cent. solution of potassium iodide and exposed to the spectrum. The result is shown in No. 1; the same rays which cause an image to be formed in the usual manner likewise caused a reversal (continuous curve, No. 1).

A plate similarly prepared was exposed in a 1 per cent. solution of potassium bromide for the same length of time, with the result that a reversal was obtained in the blue and likewise in the red, but much less marked in the latter (No. 2). These two experiments tend to prove that, in reality, it is the bromide that is acted upon to some extent,

and the effect is not entirely due to the silver-salt. This was particularly manifest in the case of the iodide and bromide slightly acidified with a mineral acid, and was much less marked when the solution was alkaline—in the latter case, the reversal taking place in the blue, and not in the red regions of the spectrum.

FIG. 14.

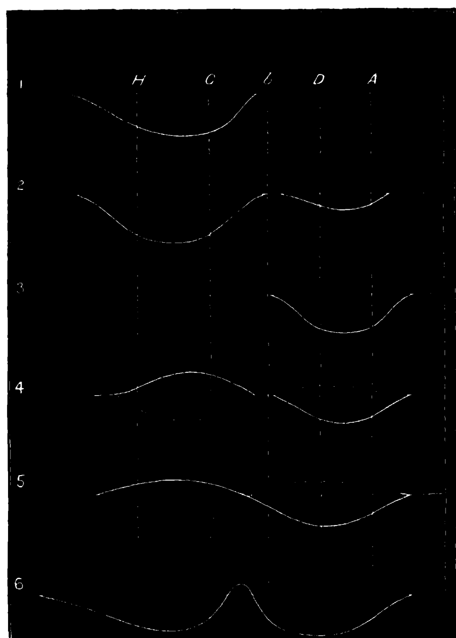


Plate showing reversing actions of iodides, bromides, and oxidising agents on silver iodide.

N.B.—The curves below the line show the reversals or positive images; the curves above the line show the ordinary action, or negative images; the ordinates approximately represent the amount of action.

To see if the silver-salt had any marked effect on the rapidity of oxidation, a silver-iodide plate was washed, given

the same preliminary exposure, and then placed in the spectro-photographic apparatus without any surrounding fluid. A reversal was obtained in the blue, but not to anything like such an extent as when placed in soluble iodides or bromides. The reversal, therefore, when the plate is exposed in the latter is partially due to the action of radiation on the bromide, and partly to that exerted on the silver-salt itself.

A silver-iodide plate, treated as before, was next exposed in a weak solution of potassium bichromate, when there was a strong reversal in the red (No. 3), and no action whatever in the blue. Permanganate of potash was next substituted for the bichromate; and the same reversing action was found, with the addition of a negative image in the blue (No. 4).

With hydroxyl the same phenomena were observed as with the permanganate, the reversal taking place a little further into the green (No. 5). Studying the absorption due to these three oxidising agents, it would appear that the reversing action *is due to the action of light on the salt of silver, which is changed by the preliminary exposure to light, and not to the action of light on the medium in which the plates are placed.*

With mineral acids a reversal was always obtained in the red and in the blue, a portion of the spectrum in the green and yellow remaining unreversed (No. 6). Now the action of these acids is not a strictly oxidising action, but is probably a removal of the loose atoms of the silver which goes to form the subiodide, and leaving silver iodide behind as the result of the action. The results of the action of acids do not, therefore, vitiate the above deduction. A plate exposed in benzene or in nitrite of potash showed no reversal even with a very prolonged exposure. It should be remarked that the action of permanganate and bichromate of potash when very dilute is sometimes to give feeble negative images in the red and blue in lieu of positive

images ; also positive images in the blue, and feeble negative images in the red (see dotted curves in Nos. 4 and 5). But this is to be accounted for by the fact that the dilution of these oxidising agents is so extreme that the reducing action on the unaltered sensitive salt is far greater than the rapidity of the oxidation.

Ordinary bromide of silver in collodion or gelatine may be taken as giving almost identical results under the influence of a soluble bromide. Now ordinary bromide is sensitive as far as B (see dotted curve, No. 7) ; and it might be presumed that this sensitiveness to the rays of lower refrangibility would cause a modification in the action of the soluble bromide. A reference to Nos. 7 and 8 will show that this is the case, but that at the same time the features which are so marked with the action of bromide on silver iodide are present. No. 7 shows the curves due to silver bromide in collodion which had received a preliminary exposure and was then exposed in a 5 per cent. solution of acid potassium bromide. It will be seen that the curves in Nos. 7 and 2 are similar, showing that the principal action is due to light acting on the soluble bromide in the presence of an acid. No. 8 is a similar plate exposed in an alkaline solution of KBr, in which there is a modification of the curve. The last loop is probably due to the silver sub-bromide itself, since the oxidation of this salt by oxidising agents occupies approximately the same position (see No. 10).

No. 9 shows the effect of permanganate of potash ; and when it is compared with No. 10, which is the curve due to oxidation by bichromate of potash, it will be manifest that the chief oxidising action lies in the red and ultra-red of the spectrum.

No. 11 also shows the effect of bichromate of potash on silver bromide after a preliminary exposure, the plate in this case being a gelatine plate. It will be seen that the bichromate totally arrests all action in the blue, whilst it rapidly causes a reversal in the red.

No. 12 shows the effect of mineral acids on silver bromide, by which it will be seen that a maximum of reversal takes place in the red and in the blue. As before

Fig. 15. B

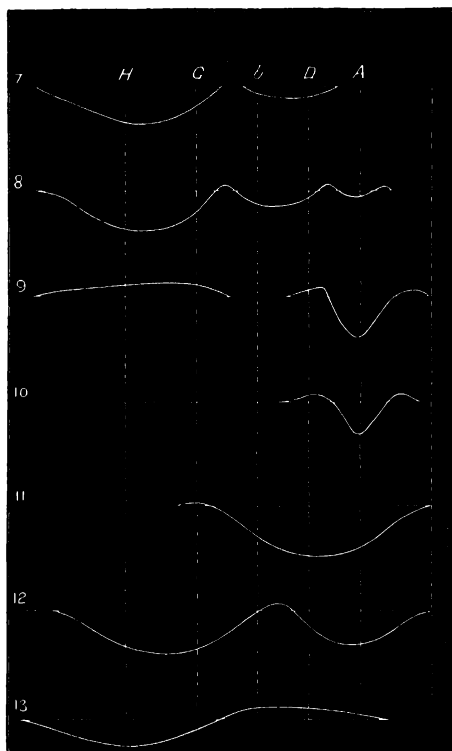


Plate showing reversing action of bromides and oxidising agents on silver haloids.

N.B.—The curves below the line show the reversals or positive images; the curves above the line show the ordinary action, or negative images; the ordinates approximately represent the amount of action.

stated in regard to the iodide, the action of these acids can scarcely be regarded as an action of oxidation.

No. 13 shows the phenomena due to over-exposure of

silver bromide, by which it will be seen that reversal takes place in the blue and not in the red. Comparing this with Nos. 7, 11, and 12, the effect of extraneous matter in causing a reversal is very marked.

Collodion plates exposed in benzene, or in aqueous solutions of pyrogallic acid, potassium nitrite, and sodium sulphite gave no reversal whatever.

Gelatine plates exposed in benzene gave the phenomena shown in No. 13, whilst with the other media no reversal at all was obtained.

The explanation of the apparent contradiction shown by the behaviour of a gelatine plate exposed in benzene has already been given.

The actions of many other liquids and gases [1] have likewise been tried; but it was thought that the examples given sufficed, since they all pointed to the same conclusions, which may be summarised as follows:

1st. The reversal of an image is due, in the majority of cases, to the oxidation of the subsalt of silver which formed by the first impact of light on the exposed salt of silver.

2nd. The oxidation is due to the action of light, the rays of lower refrangibility being the most powerful accelerators of oxidation.

3rd. Reversal of an image may be due to the presence of any haloid of an alkali, the reversal in this case being partly due to the action of light on such a haloid, and partly due to the tendency to oxidation of the subsalt of silver.

4th. The presence of a mineral acid tends powerfully to cause a reversal.

[1] Ozone was most marked in its oxidising properties, and gave a curve very similar to No. 12 both with the iodide and bromide of silver.

CHAPTER X

LIGHT FOR THE DARK ROOM

CHAP. VIII. will have paved the way for consideration of the light which is admissible in the so-called dark room.

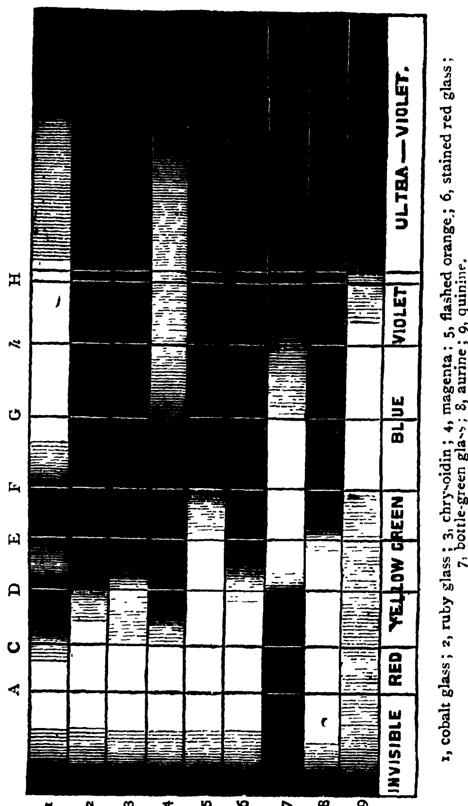
A reference to fig. 11, p. 70, will show that a gelatino-bromide plate is sensitive a very long way towards the red, starting from the blue of the spectrum.

The accompanying diagram taken from another work[1] by the author will illustrate the kind of light which comes through glasses of different kinds, together with the light which passes through certain dyes. No. 9 is added, as at one time there was an idea that a solution of quinine cut off all chemically effective light. The diagram at once disposes of this. Looking carefully at Nos. 20 and 21, in fig. 11, it will be seen that the most efficient light is that coming at the extreme red of the spectrum. No. 2, fig. 16, shows that ruby glass would be an excellent light filter were the rays in the blue absent. A combination of ruby glass No. 2 and No. 6 (stained red) accomplishes this and leaves the portion in the red alone. Stained red by itself is excellent, and there are very few plates which the light coming through this medium will affect if the exposure be not too prolonged. Stained red glass by itself allows the passage of more light altogether than does the ruby glass. The diagram on p. 100 will show the proportion of light which passes. The areas of the curves give the intensities of the lights. That of the naked light was 2639, that transmitted through orange glass 268, and that through ruby glass only 115. In other words, stained red glass only allows $\frac{1}{10}$ of the total light to pass, but ruby glass (medium) only allows about $\frac{1}{25}$. When the light is dull, as in winter, it is evident that such a diminution of light is so great that there

[1] *Instruction in Photography.* Sampson Low, Marston & Co.

will not be sufficient for the proper manipulation of plates during development, and recourse must then be had to artificial light, of which we shall presently speak.

FIG. 16.

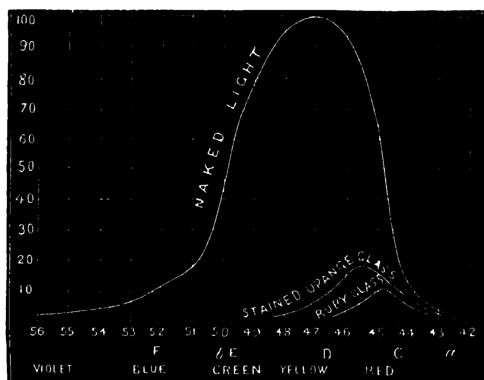


1, cobalt glass; 2, ruby glass; 3, chrysoidin; 4, magenta; 5, flashed orange; 6, stained red glass; 7, bottle-green glass; 8, aurine; 9, quinine.

Coloured glass, however, is not an essential; paper when of a proper colour and stained throughout answers equally

well, though it cuts off more of the original light. Thus a combination of chrysoidine-dyed paper and magenta-stained paper, Nos. 3 and 4, fig. 16, will be efficient. The two dyes should not be mixed, but two sheets of paper, one dyed with the one and the other with the other, should be superimposed. The worst feature in aniline dyes, however, is their certainty of fading in white light. The best medium of all is the common orange paper which is used for packing purposes. Two thicknesses of this are almost absolutely safe, and if three thicknesses be used when sunlight falls on the window there will be

Fig. 17.



no danger of veiling the plate. If thought desirable the paper may be oiled and rendered more translucent. This of course allows the passage of more light and is as safe.

Some photographers use a paper which is known as canary medium. It is paper impregnated with lead chromate and gives a pleasant whitish light. If the paper used be thin, it is not safe, since too much of the green of the spectrum passes, but if stout paper be employed it may be used with safety, since the light penetrating is small. The writer's advice is, however, to use the orange paper in preference to any other.

When artificial light is used a lantern should be constructed or purchased. There are several in the market which are satisfactory. They are usually carefully glazed, but it is no detriment if the glass breaks and has to be removed, since a piece of orange paper above alluded to can be put in its place.

A screen made by half cutting through a sheet of large cardboard at three equal intervals can be made by the amateur; the centre portion of each leaf is removed and filled in with orange paper. Such a screen folds round an ordinary chamber candlestick, and if the light striking a white ceiling be too intense, it can be cut off by placing loosely over the top a sheet of newspaper or a board. The reflection from the ceiling has never been found by the writer to hurt a plate during development, as might be expected if considered theoretically. The illumination from any source varies inversely as the square of the distance; and if the ceiling is six feet off it is illuminated only $\frac{1}{36}$ of that which a sheet of white paper would be one foot off. The ceiling becomes another source of light. It is again weakened by travelling back to operator, say another six feet. Roughly, it may be said that the illumination is $\frac{1}{200}$ of that from the light at a foot off. If one second will blacken a plate when a candle is one foot off, $\frac{1}{200}$ of a candle will not visibly affect it in the short time necessary to place the plate in the developing dish and pour over the developer. When the developer has wetted the plate it becomes comparatively insensitive.

When electric lighting is available for the dark room the lamp may be surrounded with an orange paper, and is the most charming light to work with.

For plates which are prepared with erythrosin a deep red light alone should be used; a combination of ruby glass and orange paper may be used in this case.

For the Cadett spectrum plates, which are sensitive a good way into the red, a combination of bichromate of potash and magenta dye gives a red which is practically safe.

CHAPTER XI

THE GELATINO-BROMIDE PROCESS

It would not be advisable to enter into all the various modifications which could be described regarding this process. It is thought sufficient to describe but two methods of preparation of the plates, both of which give results which cannot readily be beaten, either for rapidity or for brightness in the resulting negatives. This process is the most modern one, and its advent opened out a new era in photography, since sensitive surfaces can now be prepared which are 100 times more rapid than the older wet process which has been described. It must, however, be said that this gain in speed does not at the same time signify gain in beauty of result. For giving beautiful prints we believe some of the older processes surpass this newer one, as the negative is often much more under control as regards giving local intensity.

The gelatino-bromide process, as its name signifies, is one in which gelatine acts as the vehicle in which the sensitive salts are embedded, and it very much depends on the quality of the gelatine as to the rapidity and freedom from disfigurements which the plates prepared with it possess. The gelatine employed should be of the purest, and it should not set at too low a temperature when it is liquefied. It may be stated, as a rule, that good gelatine will absorb enough cold water to dissolve it, if the temperature is raised above 33°C. If only one quality of gelatine is to be used, Heinrich's medium hard will be found very suitable, but we prefer to mix this with Nelson's No. 1 photographic gelatine, as we shall presently describe. One fact must always be borne in mind, that frequent reheating of gelatine spoils its setting qualities; hence care must be taken as to this by keeping back a certain quantity of it during the preparation of an emulsion which requires much heating. The

sensitive salt or salts are emulsified in the gelatine very similarly in manner to their emulsification in the collodion emulsion processes described in the other chapters.

The general outline of the process is as follows:

Dissolving the soluble haloids.
Dissolving the silver nitrate in a solution of gelatine.
Emulsification of the silver haloids.
Increasing the sensitiveness by the application of heat or otherwise.
Adding gelatine to the emulsion.
Setting of the emulsion.
Washing the emulsion.
Draining the emulsion.
Cleaning the glass plates.
Coating the plates.
Drying the plates.
Packing the plates.

We shall deal with each of these operations in the order given.

First of all the following should be weighed out:

1.	Potassium iodide	·3 gramme
2.	Potassium bromide	8·7 grammes
3.	Nelson's No. 1 photographic gelatine	2 grammes
4.	Silver nitrate	11·4 grammes
5.	{ Heinrich's gelatine . . .	10 grammes
	{ Nelson's No. 1 gelatine . . .	6 grammes

Nos. 3 and 5 are covered with water, in separate vessels, and stirred to get rid of all adhering dust. Nos. 1 and 2 are dissolved in 3·5 c.c. and 40 c.c. respectively. No. 3 is swelled in 30 c.c. of water, and then dissolved by the aid of heat. No. 4 is dissolved in 15 c.c. and heated to 50°C. A drop of strong hydrochloric acid is added to the solution of No. 2. In the dark room (the lighting of which will be described in a subsequent chapter) No. 3 is added to No. 4, and shaken up in a bottle, preferably an orange-coloured hock bottle, till the mixture between the two solutions is complete. About three-quarters of the solution of No. 2 is then added drop by drop to the mixture in the bottle, and thoroughly shaken between each addition, and then with the remaining portion of No. 2 No. 1 is mixed, and the mixture added drop by drop into the bottle. If the equivalent

of the silver and haloids be calculated, it will be found that the latter are in excess. It follows from this that no combination between the silver nitrate and the gelatine can occur, since the affinity of the haloids for the silver is far greater than is that of the organic substance.

When the emulsification is complete, if a drop of the fluid be poured upon a glass plate and a candle flame be examined through it, the flame should appear ruby coloured, showing that each particle of silver is in very fine state of division. The next process is that of heating the emulsion to give sensitiveness. In the state in which it is before so doing, plates prepared with it are slow and give thin images, but after boiling great density of image is secured together with rapidity. The boiling is analogous to the ripening in the collodion emulsion processes. It is convenient to empty the emulsion out of the bottle into a flask capable of holding at least 200 c.c. of liquid, and this is placed in a saucepan of water, heated over a Bunsen burner. The flask should be placed in a jacket to prevent the access of light to the sensitive material it contains. A tin canister answers very well, if a clean cork be loosely placed in the neck of the flask. The water should be brought up to boiling-point, and kept in a state of ebullition for about forty minutes. There seems to be a time when maximum sensitiveness is arrived at, after which there is a gradual decrease in sensitiveness, and the emulsion is apt to become granular. The boiling makes the particles coarser than when the emulsion was first mixed, and on examining a drop of it on a strip of glass the transmitted colour will be found to be changed. Instead of the ruddy tint, it will appear to be bluish, with perhaps a tinge of orange in it. Whilst the boiling is taking place No. 5 should be swelled in 65 c.c. of water and dissolved by the aid of heat. It and the emulsion are then cooled down by allowing cold water to run over the flasks containing them till a temperature of about 23°C. is reached. The emulsion and the gelatine are then mixed,

and well stirred up together, so that the mass is approximately homogeneous. A white jam-pot is an excellent receptacle for the mixture, since it will then set in a solid lump and be ready for the next operation.

As far as this point the two methods are dissimilar, but henceforward the manipulations for the two are the same. We therefore shall proceed to give the alternative method of preparing the emulsion.

The same quantities of the different materials are weighed out as before, and the numbers we refer to are the same as those previously employed.

No. 1 is dissolved in 3 c.c. of water, No. 2 in 40 c.c. of water. No. 3 is soaked, swollen, and dissolved in the same water in which No. 2 is dissolved. No. 4 is dissolved in 30 c.c. of cold water, and ammonia (·880), diluted to half-strength, is added drop by drop till the oxide of silver first formed is redissolved. No. 5 is dissolved in about 60 c.c. of water. The solution of gelatine and bromide (Nos. 3 and 2) is allowed to cool to about 20°C., and then the ammonio-nitrate of silver solution is added drop by drop, with constant shaking or stirring. The iodide solution (No. 1) is finally dropped in. If the solution of No. 5 be at once added a fairly rapid emulsion will be formed, but if the emulsion be allowed to stand for from eighteen to twenty-four hours before the addition is made, a much more rapid plate can be prepared from it. The emulsion will then be grey by transmitted light. The emulsification takes place in a cool solution, and therefore there is less liability for the gelatine to be acted on injuriously by the ammonia than if heat be applied. In warm weather as much as half of No. 5 may be at once added to the emulsion to prevent its becoming granular. The emulsion is then, as in the first method, transferred to a jam-pot and allowed to set.

In hot weather it is as well to let the jam-pot and its contents stand in iced water to enable the emulsion to set rapidly and firmly. A certain amount of firmness is a

desideratum, as in the subsequent washing if only slightly set there will be too much adherent water.

The washing has next to be effected, and this can only be carried out by causing the set emulsion to be divided into very fine shreds. Squeezing the emulsion through coarse canvas, such as is used for Berlin wool work, or, better still, through mosquito netting, breaks the emulsion up to a proper state of subdivision. The contents of the jam-pot are placed in a square piece of such netting, twisted up in it, and squeezed through into a jar of water, the canvas being held beneath the surface to prevent the shreds rejoining. When all is squeezed through, the particles of gelatine may be transferred to the canvas once more, and be freely doused with water from a water-tap or by hand, and then left to soak in water for half an hour. The squeezing operation is again performed, and after another half-hour's washing the emulsion may be drained. This may be carried out by placing it on a hair sieve, or over the mosquito netting. A couple of hours' rest should render it sufficiently free from all adherent water.

The emulsion may now be retransferred to the jam-pot, which should be carefully cleaned, and then surrounded with hot water of about 30°C. till it is well dissolved. The addition of ·03 gramme of chrome alum is a safety to the emulsion. It may be dissolved in a small bulk of water and then dropped in. Next 14 c.c. of absolute alcohol are stirred into the viscid mass. If extreme rapidity be required, to the amount of emulsion here supposed to be made 10 drops of ammonia diluted with 100 of water may be stirred in, the temperature of the liquid being kept up to 33°C. for a couple of hours.

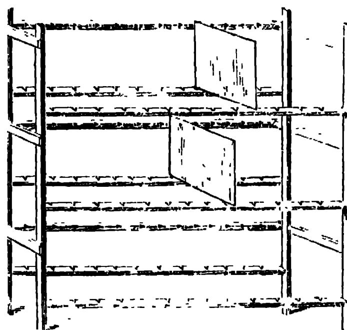
After filtering, the emulsion is now ready for coating the plates. This may be carried out by allowing it to percolate through a double thickness of swan's-down calico.

The plates are cleaned with nitric acid and water, and

then well washed in clean water. They are then dried with a clean diaper duster, and placed in a heap in the dark room for the next operation, after removing all adherent dust or fluff by a soft brush.

The emulsion, which should now be in a flask, must be kept in water of about 44°C., and, supposing a whole plate ($8\frac{1}{2}$ in. × $6\frac{1}{2}$ in.) is to be coated, about 70 c.c. of it put into a glass measure which has a lip, and a pool of the warm emulsion is poured in the centre. In fact, the plate is coated as with collodion (see p. 149), except that it is not drained so completely, a fair amount being left on the plate. The plate is next placed carefully on a perfectly level shelf of slate or thick glass, and kept there till the gelatine is set, when it is transferred to a rack such as shown in fig. 18. When the rack is full it is placed in a drying cupboard, of which there are many varieties. If a large number of plates are to be dried, a room which is dark, warmed, and well ventilated will answer, otherwise the cupboard must be resorted to. The best form of cupboard that the writer has tried is shown in fig. 19, a description of which is taken from 'Instruction in Photography.'[1]

FIG. 18.

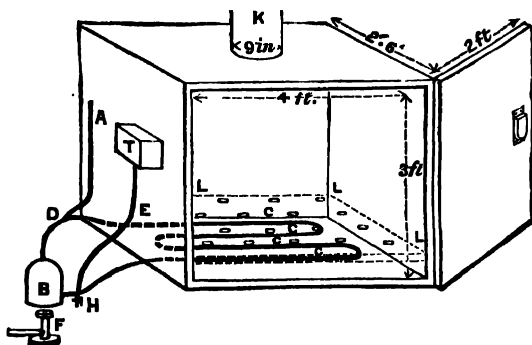


B is a zinc boiler, from which are taken two pipes, D and H, leading to the coil of pipes, C C C C. A supply tank, T, is fastened against the side of the cupboard, and a supply pipe joins the coil pipe at H. From D another pipe, A, is led, terminated with a tap, not shown on cut, which allows any air to be got rid of, which would otherwise stop the flow into C C.

[1] Sampson Low, Marston & Co.

At H is a tap, which allows the whole apparatus to be emptied at pleasure. K is a hot-air shaft, being some four feet above the box. It is terminated by a bend in two directions, and can be fitted with a cap, if required, in which are pierced orifices. Beneath are a couple of ventilating inlet pipes, likewise bent in two directions. L L L is a false bottom, pierced with holes, on which the drying racks are placed. F is a gas jet, which heats the water. (The cupboard is shown with only one door.) Each door is made light-tight by means of fillets, which need not be described. The

FIG. 19.



hinges are pianoforte hinges. The piping is made of composition gas-pipe, though perhaps iron would be better; still, as they are, they answer perfectly.

The interior of the cupboard must be maintained at a constant temperature of about 25°C., and the gas must be regulated accordingly.

A gas regulator is an excellent piece of apparatus to have to keep the cupboard up to this temperature. It must be recollected that the great desideratum in drying the plates is a constant circulation of air rather than any great heat. The plates should be dry in at least twenty-four hours,

but it is well to keep them as if drying in the cupboard for forty-eight hours, to ensure perfect desiccation.

The plates have next to be stowed away, and there is no better plan than to place them face to face in pairs, and then to make up bundles of these pairs, six plates in each, and tie them firmly together. Perfectly clean and dry pink blotting-paper may also be placed between each pair of plates, and the bundles made up as before.

CHAPTER XII

EXPOSURE AND DEVELOPMENT OF GELATINO-BROMIDE PLATES

THERE are one or two contrivances in the market which serve to indicate the speed—*i.e.* the relative sensitiveness—of a plate. Such a contrivance is Warnerke's sensitometer, which is a most useful piece of apparatus; other methods are dealt with in chap. xxxvi. A very fair judgment of the rapidity of a plate may, however, be arrived at by exposing different portions for five, ten, fifteen, &c. seconds to the light of a candle placed 12 feet off the plate. It will require a very rapid plate to show any exposure having been given to the portion which has really been exposed five seconds. The plate after preparation should never see any light which is injurious to it, and great care should be taken that in the preparation the light which must perforce fall on it is of the least hurtful colour and of a very feeble character. The same remark applies to placing the plates in the slides, and in their subsequent development.

As to exposure something must be said. The plates prepared as described in the previous chapter are exquisitely sensitive to white light. With a rapid rectilinear lens by Dallmeyer, using the smallest stop (No. 5), an open landscape on a bright spring day is impressed in half a

second, always supposing there are no very near deep shadows, which will require a slightly longer exposure to bring out detail in them.

With these particular plates, when they are covered fairly thick with emulsion, the exposure may be prolonged to three seconds under the same circumstances without any detriment to the resulting negative. This is what is technically called latitude of exposure. A negative with such a prolonged exposure requires care in development, but all details in every part of the picture can be brought out without difficulty if proper precautions are used. With a larger stop, say No. 3, which is usually small enough to place the whole of a picture in good focus, only a quarter of the above exposure need be given, which is about one-eighth of a second. For such exposures 'uncapping the lens' is impracticable, and resort must be had to some sort of mechanical shutter, a description of some of which will be found in a subsequent chapter, as will be the choosing of the picture.

When the slides containing the plates are carried to the camera they should be shielded from light, and the front board of the slide should only be withdrawn when the focussing cloth is thrown over the camera, also to protect it from light.

Light usually enters a lens through the slots which are cut in the brass mounts for the diaphragms or stops. This orifice should be covered over with an india-rubber band. It also frequently happens that the light coming through the lens is reflected on to the sides of the camera. This may be overcome by placing an oblong diaphragm behind the lens with an opening in it just large enough to cut off all light which does not fall on the plate. The inside of the camera should be of a dead black, and, in fine, too much care cannot be taken to ensure the absence of all reflections.

For developing these plates there are almost innumerable formulæ, but the writer gives two for alkaline development which he has found work really well with him, and also one for ferrous oxalate.

The first formula stands thus :

1.	Pyrogallic acid	Dry
2.	Potassium bromide	40 grammes
	Water	1 litre
3.	Ammonia (·880)	1 part
	Water	9 parts
4.	Sodium sulphite	A saturated solution in water

For developing a plate we usually commence by taking the following proportions :

No. 3	4 c.c.
No. 2	4 c.c.
No. 4	4 c.c.
No. 1	·2 gramme

The amount of No. 1 is not necessarily very exact, provided there be sufficient of it present, and it can be approximately judged after a few trials. A useful piece of apparatus is a bone or horn spoon to act as a dry measure for it.

The above are mixed together, and then made with water to 60 c.c. This quantity will be found sufficient with which to develop a 'whole plate.'

The plate, having been taken out of the slide, should be carefully dusted with a broad soft brush and laid in a dish very slightly larger than the plate.

The developing solution should then, with an even sweep, be made to flow over the plate, care being taken that no bubbles form on the surface. Should a bubble appear it must be broken at once with the finger, or with a brush kept for the purpose. The appearance of the image should be watched. If it begin to appear in ten seconds, the developer may be kept in motion over the plate, and the image be brought out with the strength of developer given above, until the highest lights appear as blackish patches at the back of the plate when viewed by reflected light. Should the image not appear in twenty seconds, 2 more c.c. of No. 3 should be added, when, if the exposure

be anything approaching that necessary, the image should be rapidly brought out and gain density. Should it appear that the density necessary to give the highest light will be arrived at before the whole of the detail in the shadows is out, it is an excellent plan to pour back the developer into the cup, and allow the image to come out under the influence of the developer which is absorbed in the film. The rationale of this is that the developer soon exhausts itself in the parts of greatest density, whilst it is almost unaltered in the parts where no detail has put in an appearance. When the detail has been brought out in this manner, the image should be intensified by a fresh application of the developer.

In the case of so-called instantaneous pictures, when exposure has been excessively short, it is a good plan to soak the plate in 3 c.c. of No. 3 and 60 c.c. of water, and after a couple of minutes to add to the developing cup the proportions above indicated of Nos. 1, 2, and 4. This will cause what would otherwise be an under-exposed picture to develop as if it had received a longer exposure.

Another developer which the writer can recommend from personal experience is as follows :

1.	Potassium carbonate, pure . . .	3 parts
	Water	8 parts
2.	Potassium bromide	1 part
	Water	25 parts
3.	Pyrogallic acid	Dry
4.	A saturated solution of sulphite of soda in water	

3½ c.c. of No. 1, ·5 c.c. of No. 2, ·2 gramme of No. 3, and 4 c.c. of No. 4 are mixed, and made up with water to 70 c.c. and applied. This is a normal developer. The writer prefers to commence with 2 c.c. of No. 1, with the same amounts of Nos. 2, 3, and 4, and to add more of No. 1 if required. For instantaneous pictures the plate may first be soaked in 3½ c.c. of No. 1 and 60 c.c. of water, and the bromide, sulphite, and pyrogallic acid subsequently added.

Negatives developed with this developer are delicate, but the density may be increased by a final addition of 2 drops of ammonia, ·880. The ferrous oxalate developer may also be used as prepared at p. 169. The writer recommends that it should be used of half-strength (*i.e.* diluted with water) till all the detail appears, after which a fresh quantity of the strong developer is applied, to which 1 c.c. of a 2·5 per cent. solution of potassium bromide is added. This will bring up the negative to the necessary density.

In the case of instantaneous pictures the developer should, as before, be used half-strength, but an addition to every 50 c.c. of 20 drops of a 2·5 per cent. solution of hyposulphite of soda in water should be made. This addition gives marvellous developing properties to the ferrous oxalate, increasing its power three- or four-fold.

There are several developers which should be mentioned in reference to the development of gelatine dry plates, all of which are excellent. The earliest in point of date, after the pyrogallic acid and ferrous oxalate developers, is the hydrokinone, which was discovered by the author. It gives a beautifully coloured image and develops very cleanly.

Three modifications are given.

The following solutions are prepared :

A	Hydrokinone	4 parts
	Water	1,750 parts
B	Ammonia	50 parts
	Water	500 parts

To every 30 parts of A one part of B is added, to obtain full intensity. The ammonia may be added gradually, beginning with a quarter of the quantity at first.

Another modification is :

C	Hydrokinone	2 parts
	Water	500 parts
D	A saturated solution of carbonate of potash in water	

To every 8 parts of C one part of D is added, and about ⅛th part of a 2 per cent. solution of sodium chloride. Some

photographers use sulphite with the solutions, and the following is very good for instantaneous photographs:

E	Hydrokinone	100 parts
	Meta-bisulphite of potash, or sulphite of soda	100 parts
	Water	5,000 parts
F	Sodium hydrate	50 parts
	Water	100 parts

One part of E is mixed with one part of F.

With all these forms of hydrokinone developer the image should appear rapidly. In cases of strong contrast the solution containing the hydrokinone should be reduced to half the amounts given above. The addition of bromide as a restrainer is not recommended, as it is too powerful. If any restrainer be required, the addition of a small quantity of a saturated solution of common salt is recommended.

Eikonogen.—Eikonogen is a developing compound which is a very general favourite. It gives a soft, graduated picture, and brings out all detail possible before the density becomes too great in the high lights. The following formulæ can be used:

Eikonogen	10 parts
Sodium sulphite	20 parts
Sodium carbonate	10 parts
Potassium bromide	·5 part
Water	400 parts

or

Eikonogen	25 parts
Sodium sulphite	50 parts
Sodium carbonate	50 parts
Potassium bromide	·5 part
Water	1,000 parts

These are 'one-solution' developers, but if two solutions are required, half the water may be added to the eikonogen and sodium sulphite, the remaining half being reserved for the other constituents. When this is done, detail can be

obtained by adding more alkali, and less density by diluting the eikonogen.

A very convenient form of eikonogen developer is supplied by photographic chemists in the shape of cartridges containing all the above ingredients in proper proportions with the exception of the bromide. A cartridge is directed to be dissolved in 100 c.c. of water, but we have found it better to use 150 c.c. instead.

Amidol.—There is one more developer which is to be highly recommended, viz. amidol. It gives a beautiful black image, and is rapid in its action, more especially when used strong. The following may be used :

Amidol	20 parts
Sodium sulphite	150 parts
Potassium bromide	2 parts
Water	2,500 parts

It will be seen that no alkali is required with this developer, there being sufficient alkalinity in the sulphite for the purpose. It is best to dissolve the sodium sulphite first in the water, and then to add the other ingredients. Amidol will not keep long, and should be made up fresh. The solution in time becomes very dark, and in this condition is not so active as in the colourless state. It may be used whilst light-coloured over and over again.

Eikonogen will keep for weeks when made up, and retains its energy till it becomes decidedly fluorescent.

Hydrokinone is best made up as required, as it becomes brown by keeping, though the sulphite of soda preserves it when this is used with it.

Metol.—Metol gives a good black image, but to ensure full density development must be carried on for some time after the image has appeared. As it works best in conjunction with large quantities of sodium sulphite, the amounts given in the maker's formulæ may be increased

with advantage. The following is a good formula for normal subjects:

Metol	2 parts
Sodium carbonate	20 parts
Potassium bromide	½ part
Water up to	400 parts

As much sodium sulphite as is practicable should first be dissolved in the water.

Glycin.—This developing agent gives full density with clear shadows, and is well suited for line negatives on dry plates. A good working solution is:

Glycin	4½ parts
Sodium sulphite	13 parts
Potassium carbonate	21 parts
Water	400 parts

The sulphite is first dissolved in hot water, and the glycin and the carbonate added while the solution is still warm. Potassium bromide is not absolutely necessary with correctly exposed plates, and even with over-exposed plates it should be added cautiously, as it has considerable retarding effects upon development.

Para-amido-phenol or Rodinal.—Rodinal is the commercial name for the concentrated solution, in which form para-amido-phenol is sold. For use it should be diluted with from twenty to thirty times its bulk of water. As with amidol and metol, the image appears quickly, but gains density slowly. Bromide does not restrain so powerfully as with glycin, and may be freely used.

Diphenol is also sold in solution, and is diluted for use—1 part to 8 parts of water for over-exposure, 1 part to 15 parts of water for correct exposure, and 1 part to 25 parts of water for under-exposure.

Ortol.--Ortol has no developing power by itself. Combined with sulphite it will develop slowly ; with the addition of sodium carbonate development takes place rapidly and steadily, yielding a black image. Mr. Bothamley gives the following formula :

Ortol	3½ grains
Potassium meta-bisulphite	2 grains
Sodium carbonate . . .	25 grains
Potassium bromide	½ grain
Sodium sulphite	12 grains
Water	1 ounce

with an increase in the bromide for rapid plates and for over-exposure.

Adurol.—Adurol keeps well both in the dry state and in solution ; it yields negatives of excellent gradation and vigour, of a good black colour. A small quantity of bromide will check all tendency to fog, even with rapid plates and over-exposure. A developer for normal subjects would contain

Adurol	4 parts
Sodium sulphite	20 parts
Potassium carbonate . . .	24 parts
Potassium bromide	¼ part
Water	400 parts

Kachin.—Kachin gives negatives of a good brown-black, and does not stain the fingers or nails ; it keeps well in the dry state, and in solution with the amount of sulphite recommended by the makers. Their latest formula is :

Kachin	4 grains
Sodium sulphite	27 grains
Sodium carbonate	22 grains
Water	1 ounce

with the addition of one or two drops of a 5 per cent. solution of borax in cases of over-exposure.

The plate after development must be well washed, and should be fixed in a bath of hyposulphite of soda, one part, in water five parts. Films containing much iodide take somewhat long to fix, *especially* if the emulsion has been prepared by the ammonia process. The plate should be thoroughly washed for a couple of hours in constant changes of water. When the film is tender, and has a tendency to leave the plate, between the developing and fixing operations it should be immersed for five minutes in a saturated solution of alum, the film being washed both before and after the immersion. When finally drying the negative care should be taken that no drops of water are left on the film, as they are apt to cause marks. Our advice is to sponge the surface of the negative with a very soft sponge before it is dried. Over-exposed pictures, and pictures taken on plates on which the layer of emulsion is small (as in some cheap commercial plates), will be found to lack density, and they must be intensified. Unfortunately the film of gelatine almost precludes the intensification being carried out as for wet plates, owing to the gelatine staining. Resort is therefore had to mercury intensification, and it is believed that the two following are permanent.

The following solutions are prepared :

1.	Mercuric chloride	6 grammes
	Potassium bromide . .	6 grammes
	Water	300 c.c.
2.	Silver nitrate	6 grammes
	Water	300 c.c.

To No. 2 is added a 20 per cent. solution of potassium cyanide in water, till the precipitate of cyanide of silver first thrown down is very nearly redissolved. The solutions are filtered.

To intensify an image, the plate when dry is immersed in water for five minutes, and placed in a dish containing No. 1. Here it is allowed to bleach thoroughly. It is then washed in running water (or constant changes of water) for

a quarter of an hour, when it is placed in a dish containing No. 2. The image immediately takes a black colour and becomes dense. The film must be next thoroughly washed. It may happen that the density is too great, in which case it can be reduced by immersion in a 4 per cent. solution of sodium hyposulphite.

Intensifier.—A very useful intensifier, and one which Mr. Chapman Jones has studied, is as follows: The negative is fixed, and after fixing is well washed and treated with alum to remove any trace of hyposulphite of soda. It is then bleached in a saturated solution of mercuric chloride, to which a drop or two of hydrochloric acid is added, and again thoroughly washed until it begins to turn a shade of brown. It is then treated with ordinary ferrous oxalate solution, or with one of the above developers which does not contain ammonia, when the bleaching disappears, and gives place to an image formed of metallic silver and mercury in combination. This process may be repeated over and over again till the required density is obtained.

Success in this mode of intensification depends on the thoroughness of the elimination of hyposulphite of soda and the washing of the bleached image. The image can be relied upon as being permanent. This takes a longer time to carry out than the other methods given, but if the manipulator be careful it will always be successful.

Before the negative is taken into regular use for printing it should be varnished. Celluloid or lac varnish will answer, and the manipulations given at p. 158 should be followed.

Defects in Gelatine Negatives

The worst defect of all, but fortunately one not frequently met with in modern plates, is the tendency of the film to leave the plate. This is usually cured by immersion in the alum bath between fixing and developing, as it generally happens that this 'frilling' of the plate takes place in the

hyposulphite of soda solution. A badly cleaned plate is also conducive of frilling, for which there is no cure.

Blisters are usually followed by frilling, and what applies to it applies to them. Green fog is seen when alkaline development is employed; the emulsion from which the plates are prepared is then at fault.

General fog is usually due to the emulsion, but when it is not very bad the plates may be used by giving slightly prolonged exposure and adding treble the amount of potassium bromide solution prescribed for the alkaline developer. Yellow or brown stain all over the negative is often seen after alkaline development. It may be got rid of by soaking the plate in a 1 per cent. solution of hydrochloric acid in water. It is safer instead of the water to use a saturated solution of alum, and to add the hydrochloric acid to that. This prevents any chance of blistering or frilling.

Opaque spots are usually due to dust on the plate, which settles during drying or before exposure.

Transparent spots are due to the use of gelatine in which there is a small amount of greasy matter, or to fungoid growth in the gelatine whilst the plates are being made.

Transparent pinholes on the negative after fixing may be due to dust on the plate, probably entering the dark slides. This can be avoided by rubbing the dark slides with a little glycerine. The glycerine acts as a trap to the dust.

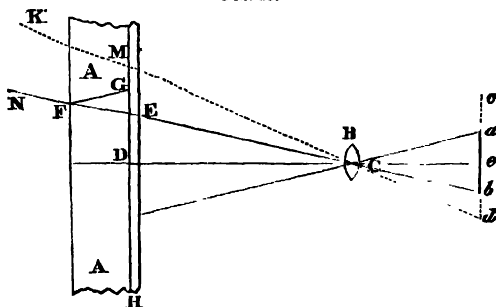
Dark lines on the negative are often due to the scratching of the film by some rough substance before development. The scratching seems to decompose the silver salt in a similar way to light.

A want of sharpness in a picture may be due to inaccurate focussing, to a want of achromatism in the lens, or to the camera being shaken accidentally by the wind, or by the sinking of the camera legs during the exposure. If the lens be in fault there is no help for it but by ascertaining how much further backwards or forwards the ground glass of the

camera ought to be shifted in order to get the sharpest result possible. This can easily be found by actual trial, and when noted the ground glass may be permanently placed in such a position relatively to the glass plate in the dark slide, that when the picture is visually in focus the position of the sensitive plate shall be chemically in focus.

A blurring of the image can easily be accounted for; though, perhaps, there has been more controversy on the subject than on any other photographic phenomenon. It is usually ascribed to geometrical reflections of the incident rays coming through the lens from the back surface of the

FIG. 20.



glass, and no doubt, in some cases, this is absolutely true, though in others it requires a more complete explanation. It must be borne in mind that the rays of light do not strike the surface of the plate perpendicularly except at its centre. The accompanying diagram shows a glass plate, A A, of exaggerated section, with rays of light passing through the optical centre, C, of the lens, B, coming from a bright line, *a b*. The ray *e* C D is perpendicular, and the ray *b* C E makes an angle with the perpendicular. This last ray, after passing through the film (which for the time we may consider transparent) would be bent inwards to F, and a portion would be reflected from the back surface of the plate, and strike the thin collodion film again at G. From G a

portion might be reflected again, and so on. Evidently, in this case, a blurring might take place, but always *outwards* from the centre of the plate. If, however, the ray of light *b* C E proceeded from the extremity, *b*, of the dotted line, *b d*, which may be supposed to represent a bright line of light, then no blurring would be apparent, as the blur from it would be covered by the image E M, of the bright line. Now in practice blurring is usually most intense when a dark object, such as a tree, is opposed to a bright object, such as the sky; in which case we may suppose *b d* to be a section of the sky, and *a b* of the tree, which we may suppose to be a dark line in section. Here the blurring is evidently not due to reflections of the incident rays from the glass. To account for it, we must look to another feature of the sensitive surface. If a sensitised film be examined under the microscope it will be found to consist of minute grains of silver bromide, iodide, or bromo-iodide, and each of these grains individually must reflect more or less light from its surface. A beam of light, therefore, must be dispersed in every direction, and, as has been shown,[1] the light striking at any point of the film is scattered and reaches the back surface of the plate as a disc, with intensity gradually diminishing from the centre. The reflection from that surface becomes most noticeable when the critical angle of the glass is reached. The direction that the rays take in striking the particles is not of any great moment, as the difference in intensity of the reflections in any one direction is very slight when the angle does not differ very largely from a right angle. Hence it is seen that blurring really takes place from this cause in all parts of a picture taken on a glass plate, but that it is naturally most apparent when a bright light is opposed to a deep shade. There is still another point in this particular scattering of the rays to take into account, and that is, the lateral scattering. Supposing the intensity

[1] See *London, Edinburgh, and Dublin Phil. Mag.* January 1875.

of the light in the lateral direction to be only $\frac{1}{100}$ of that in the perpendicular, the penetration into the film would still be considerable, and a blurring would result on this account. In photographing fine lines close together this kind of blurring is often most apparent, a black line being often filled up, or rendered too fine. It has been argued that blurring is also due to the lens, but a serious consideration of the matter will show that such an effect is hardly possible if it be tolerably achromatic.

The blurring caused by the reflection of the scattered rays from the plate can be almost entirely destroyed by placing a backing of some black or non-actinic colour in optical contact with the back surface. Asphaltum dissolved in benzene is perhaps the most effective backing to use.

CHAPTER XIII

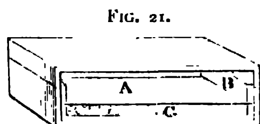
THE DAGUERREOTYPE

HAVING described the process at present in use, it is proposed to treat of the other processes, but for reasons they are not taken in strictly historical order. The first is that due to Daguerre. It is even at the present date occasionally adopted for some kinds of work.

The daguerreotype process consists, as already stated, of the formation of a sensitive surface of silver iodide, or silver iodide and bromide, on a silvered plate, by means of the direct action of iodine, or iodine and bromine. One of the most difficult (and difficult only because the greatest cleanliness in every detail is required) parts of the whole process is the preparation of the silvered surface before its coming in contact with the halogen. The plates are usually copper, on which a film of metallic silver is deposited by the electroplating process, and when they leave the silvering solution have, as a rule, a frosted appearance. After being cut to

the proper size, and the corners clipped off about one-eighth of an inch for convenience' sake, they are ready for polishing. A plate in this state may be placed on a flat table, and four thin strips of wood nailed round it to prevent it slipping. To the surface is then applied tripoli powder in alcohol with Canton flannel, and worked about to such an extent that it is perfectly free from scratches, and is fairly smooth. The next operation consists in polishing it. This is effected by means of a buff. That which the writer has found effective is made by enclosing a wooden ball, of the size of a small apple, in a skin of felt and then of cotton wool. Over this is stretched a piece of the finest chamois leather. On to the surface of the silver is then scattered a small quantity of jeweller's rouge, and the buff is caused to travel over the plate from end to end and side to side alternately till it becomes of the highest polish. This polishing should take place almost immediately before the sensitising operation is commenced, otherwise there is a liability of the surface attracting impurities from the atmosphere. To sensitise the plate two sensitising boxes are required. An illustration of that employed when daguerreotype was commonly practised for portrait work will give an idea of the sort of contrivance required. On the bottom of the box C is placed iodine in powder; A is a piece of cardboard, which fits into grooves as shown. B B are the supports on which the silvered plate is to rest.[1] The iodine will volatilise at ordinary temperatures, and condense on the surface of the cardboard next to it. When a plate is to be sensitised the cardboard is reversed, and the iodine volatilises from the top surface on to the silver plate. The plate gradually receives a thin coating of iodide, passing through

FIG. 21.



[1] When smaller sizes are to be used they may be held in frames similar to the inner frames of a camera slide.

various stages of colour. When a ruddy colour is reached, it is placed in a similar box to that already described (omitting the cardboard), at the bottom of which is a mixture of bromine and calcium hydrate. The bromine attacks the surface, and with the iodide forms silver bromo-iodide. When the surface assumes a steel-grey or violet colour the plate is removed, and once more placed in the iodine box for a third of the time originally necessary. In this state the plate is exceedingly sensitive, and is ready for exposure in the camera. The exposure may be made at once, or it need not take place for several hours; Claudet, in fact, found that, by keeping, the sensitiveness increased. The time necessary to impress an invisible but developable image is very short, a few seconds being all that is necessary. Practice alone can tell the exact time required, but it is soon learned approximately after a few trials. The development is accomplished by exposing the impressed surface to the vapour of mercury. A cast-iron tray, with wooden sides and lid, is convenient: it may form a box similar to that shown for the iodising operation. At the bottom is placed a thin layer of mercury, the temperature of which is raised to about 150° F. The plate is placed in the box, face downwards, on the supports, and the development is allowed to proceed, the process being watched as it progresses by inspecting it from time to time in a non-actinic light. If the exposure be right the image will be brilliant, if under exposed it will be weak; whilst if over-exposed it will be covered with a veil of mercury.

The development, it will be remarked, is due to the attraction of the subiodide for the metallic mercury vapour, and to no other cause. In order to fix the image the plate is immersed in a 10 per cent. solution of sodium hyposulphite. After a few seconds the unaltered iodide Ag_2I_2 and the AgI of the subiodide (Ag_2I) are dissolved away, and the image is left as a white amalgam of mercury and silver on a darker-coloured background. After a thorough

washing in distilled water the picture is permanent, but its appearance may be improved by toning it; *i.e.* intensifying it with gold to darken the silver, and render the amalgam still purer in colour. This is accomplished by pouring over it, in such a quantity as just not to run over the edges,

1.	Gold trichloride	·1 gramme
	Distilled water	50 c.c.
2.	Sodium hyposulphite	·4 gramme
	Distilled water	50 c.c.

The two solutions are well mixed together, and, after flowing them on the plate, a spirit-lamp is moved about beneath its bottom surface until the toning action commences. The more rapid the deposition of the gold, the more satisfactory the image. When complete, the plate must be well washed in a dish of cold water, and finally rinsed with distilled water. Drying is best accomplished by gentle heat, applied first at one end, and gradually moved down. Any large drops of water should be absorbed by blotting-paper.

Daguerreotypes may be reproduced by electrotypy, if the plate be immersed almost immediately after toning in the copper solution. The ordinary electrotyping process answers every purpose: for the details, reference must be made to books treating specially of the subject. The fact is mentioned here, as it shows that the image, after all these operations, is *in relief*, though naturally to a very limited extent, yet still sufficiently to cause the reflected light to give all the necessary gradations of light and shade. Sir W. Grove also introduced a method of etching daguerreotype plates by means of the battery. He immersed the plate in a solution of hydrochloric acid two parts, and water one part, and opposed by a platinum plate placed at ·2 inch from it. When the current was generated by a couple of Grove's cells, an oxy-chloride of silver was formed, and after thirty seconds the plate was found to

be sufficiently bitten. The oxy-chloride was removed, and for *fine* work was found of sufficient depth to allow it to be printed from with printer's ink in the printing-press. This process has not come much into vogue, as it is one which is too delicate for ordinary operations, and the silvered copper is expensive in comparison with the other metals employed for the purpose. The most recent development of photo-engraving and the production of reliefs are described in a subsequent chapter.

CHAPTER XIV

COLLODION

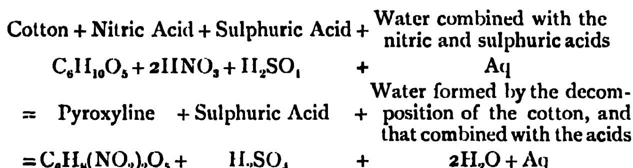
PYROXYLINE[1] is prepared by acting upon cotton, paper, or other kindred substances with a mixture of nitric and sulphuric acids. For an example of the process we may take cotton, which has a definite formula of $C_6H_{10}O_5$. Sulphuric acid has the property of absorbing water from any organic substance with which it is in contact; for instance, a drop of oil of vitriol on cloth or paper rapidly chars it, owing to the destruction of the constituent atoms, through the affinity of oil of vitriol for water. Thus, if we take the cotton itself, it will be seen that each molecule contains 6 equivalents of carbon, and just sufficient hydrogen and oxygen to form 5 molecules of water; the oil of vitriol is thus capable of splitting up the molecule of cotton, appropriating the 5 molecules of water, and leaving the carbon behind. Another good example of the abstraction of an equivalent of water from a molecule is in that of ethyl alcohol, or spirits of wine. If this be distilled over in the presence of concentrated sulphuric acid, we have ether[2] as the product. When the acid is diluted

[1] As collodion is seldom used it may be well to keep a record of its manufacture for the benefit of workers who may require to make it.

[2] Ethyl Alcohol = Ether + Water abstracted by the sulphuric acid
$C_4H_{12}O_2 = C_4H_{10}O + H_2O$

with water, its destructive power is limited, though as the water evaporates from it the power returns.[1]

Now the strongest nitric acid which is usually obtainable contains a large proportion of water. Thus nitric acid of 1·457 sp. gr. at 60°F. contains only 84 per cent. of HNO_3, hence it is that when this is mixed with sulphuric acid the water is abstracted from it, and the true nitric acid (HNO_3) is left to act on any body with which it is brought in contact. This is undiluted, and is capable of acting on cotton in a somewhat peculiar way. It abstracts either 2 or 3 atoms of hydrogen (according to the strength of the acids employed, and the temperature), and replaces them by 2 or 3 molecules of nitrogen tetroxide (NO_2) with the formation of water. The formula stands thus :



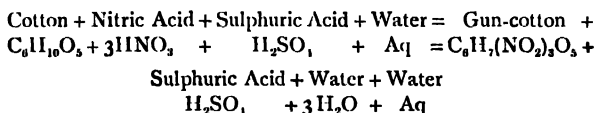
Cotton + Nitric Acid + Sulphuric Acid + Water combined with the nitric and sulphuric acids

$C_6H_{10}O_5 + 2HNO_3 + H_2SO_4$ + Aq

= Pyroxyline + Sulphuric Acid + Water formed by the decomposition of the cotton, and that combined with the acids

$= C_6H_8(NO_2)_2O_5 + H_2SO_4 + 2H_2O + Aq$

or,



Cotton + Nitric Acid + Sulphuric Acid + Water = Gun-cotton +

$C_6H_{10}O_5 + 3HNO_3 + H_2SO_4 + Aq = C_6H_7(NO_2)_3O_5 +$

Sulphuric Acid + Water + Water

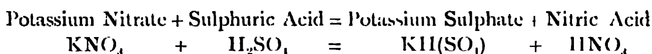
$H_2SO_4 + 3H_2O + Aq$

The first being the gun-cotton, as used for collodion, and the second being the well-known explosive compound. It will be noticed that the sulphuric acid remains unaltered in composition, its sole function being to absorb the water formed by the operation. The fact of the existence of the tetroxide of nitrogen in the altered cotton can be demon-

[1] It is for this reason that if the most dilute sulphuric acid be spilt on the clothes, or passed through a filter-paper, and be allowed to dry, a charring takes place. In the first case neutralisation with an alkali, or in the second very thorough washing, will prevent the disaster.

strated in its combustion in an exhausted glass vessel by the red fumes which tinge the gaseous products.

The same reaction as the above can be obtained by employing potassium nitrate (KNO_3) instead of the nitric acid, though in this case a portion of the sulphuric acid becomes converted into potassium sulphate. Thus:



Potassium Nitrate + Sulphuric Acid = Potassium Sulphate + Nitric Acid

$$KNO_3 \quad + \quad H_2SO_4 \quad = \quad KH(SO_4) \quad + \quad HNO_3$$

The above equations represent the reaction that theoretically takes place when cotton is treated with nitric and sulphuric acid in the above proportions, but there are other points to be attended to in practice.

The proportion of the acids to each other materially affects the properties of the pyroxyline. Sulphuric acid parchmentises paper when it is immersed in it or floated in it, that is, renders it tough and of close texture. The chemical effect produced by the sulphuric acid is hardly known, but if prolonged, it is known that the paper is dissolved. Parchmentised paper treated with nitro-sulphuric acid has different qualities from that in which the parchmentising is omitted. With the former a tough collodion results, though it is more powdery. An excess of sulphuric acid beyond that necessary to produce the reaction shown in the equations acts in a similar way to treating the cotton first with the acid, for it partially parchmentises the cotton previous to its conversion into pyroxyline, and as this is beneficial to a collodion, when not carried beyond proper limits, an excess of this acid is always employed.

The amount of dilution of the acids with water also largely modifies the resulting compound. When little or no water is added, the pyroxyline gives an unevenly flowing collodion which is strongly contractile when drying. When a large proportion of water is added, the collodion is limpid, flows readily, and is apt to give a matt appearance on drying. By increasing still further the amount of water, the cotton

when immersed will entirely dissolve in the acids. Evidently then a mean between no water and the amount necessary to produce dissolution should be employed.

The effect of the temperature of the acids on the cotton is also marked by the behaviour of the resulting pyroxyline, as the effect of heat is to aid chemical change. Pyroxyline made at low temperatures forms a collodion that is always glutinous and difficult to flow over a plate, whilst the higher the temperature the more easily will it flow. It should be remarked that the same effect is produced by the addition of more or less water to the acids. It is, therefore, possible by diminishing the amount of water and increasing the temperature to obtain the same amount of fluidity in a collodion as would be gained by the full amount of water at a lower temperature.

With the above facts before us we can evidently manufacture various qualities of pyroxyline which may be suitable for different purposes. With the wet process, where a solution of silver nitrate comes in contact with the soluble iodides, &c., dissolved in the collodion, its conditions should be: Firstly, that it should be fairly porous; and, secondly, that it should be fairly tough. This is effected by adding a moderate proportion of water to the mixed acids, and by immersing the cotton in it at a medium temperature.

The following are the proportions which Hardwich (who was the first to thoroughly investigate the manufacture of pyroxyline fit for collodion) states should be observed:

Sulphuric acid, sp. gr. 1·842 at 15° C. .	500 c.c.
Nitric acid, sp. gr. 1·456	166·6 c.c.
Water	145·7 c.c.

The nitric acid and water are first poured into a strong glazed porcelain dish, and well mixed, the sulphuric acid is added last, the liquid being kept well stirred as it is poured in. The temperature will generally rise to 75° or 85° (if to the latter, it may be suspected that the acids are too dilute), and it must then be allowed to cool gradually to 65°. A

dozen balls of cotton wool,[1] weighing about 1½ gramme each, having been prepared, should be immersed separately in the fluid, and after thorough soaking (assisted by a glass or porcelain spatula, fig. 22), be allowed to remain at the bottom of the vessel. The immersion should take place rapidly, otherwise decomposition takes place, and this, when once commenced, will cause the temperature to rise rapidly, and the whole of the cotton will be dissolved with the evolution of nitrous fumes. The balls must be left in the acid from ten minutes to a quarter of an hour, and they are then presumably in a state ready for washing. The longer the immersion, the more likely are they to become insoluble in ether and alcohol, approaching more nearly the state of explosive gun-cotton. They are next raised by the spatula, the excess[2] of acid as far as possible squeezed out of them against the side of the vessel, and then they are dashed into a vessel holding a large quantity of water. All traces of the acids are eliminated by washing in frequent changes of water, or, better still, in running water. To test when this is complete, a piece of blue litmus-paper should be pressed against the wet cotton, and if after two minutes it remains unaltered it may be assumed that the washing is complete. The pyroxyline should now tear easily, and not be readily separable into the original balls, and should weigh about 30 grammes. If the original fibre be easily distinguishable, the temperature probably fell during the operation, or sufficient water was not added. If the weight fall much below that indicated, the water was probably a little in excess, or the temperature was too great. It cannot be too strongly impressed upon the student that the strength of acids is all-important, and if the amount of water present with them be above that indicated, that so much water must be deducted from that given in the formula. A specific

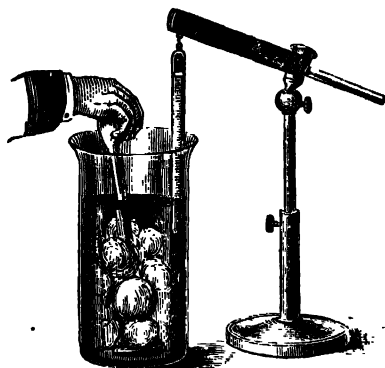
[1] The cotton should have previously been well steeped in soda and water, and be then *thoroughly* washed and *completely* dried.

[2] If the precaution be not taken of squeezing out the acids, there is a great probability of a solution of a portion of the cotton taking place.

gravity bottle is a very convenient means of ascertaining the strength of the solution, for, the specific gravity once known, the amount of true acid present can be found from the tables given in the Appendix. Other methods for ascertaining the specific gravity will be found in most works on chemistry.

The next formula for preparing pyroxyline of the same character is given without comment, as the above remarks apply to it.

Sulphuric acid, 1·842	170 c.c.
Dried potassium nitrate[1] . . .	110 grammes
Water	28·3 c.c.
Best dried cotton wool . .	4 grammes



Hardwich states that the chances of failure with this process are very slight if the potassium nitrate be not too much contaminated with potassium chloride. In the above operations a thermometer is absolutely necessary. It should not be mounted in wood, but should be graduated on the stem itself. It may be supported in a clamp, as shown in the figure. For dry processes the foregoing formulæ give

[1] The potassium nitrate should be dried at a temperature of about 120°. Placing it in an air-bath is the most convenient method of obtaining the temperature.

pyroxyline, which some consider as too tough and horny, and some hold, though the writer does not, that this is especially the case for processes where the sensitive salt of silver is formed in the collodion itself (see chap. xviii.). A modification in the proportions of acid and water can be made to suit those who prefer a more limpid collodion. It has also been found by some workers that in the latter process the presence of a little nitro-glucose is a desideratum. The following method secures its formation, though, if the resulting pyroxyline be well washed, it is in a great measure eliminated. It would seem better to add the nitro-glucose to the collodion, but as this has not been established from long experience, it has been thought better to give the process as published by M. Léon Warnerke, in a communication to the Photographic Society of Great Britain. Six grammes of the finest cotton wool are put into a porcelain jar, and 2 grammes of gelatine dissolved in the smallest quantity of water are added. The cotton is impregnated with the gelatine by pressing it with a wooden spatula, and when this is effected the cotton is carefully dried by the aid of heat. It is then ready for immersion in acids which are of the following strength :

Nitric acid, 1·45	175 c.c.
Water	68·3 c.c.
Sulphuric acid, 1·840	262·5 c.c.

or,

Nitric acid, 1·42	194·1 c.c.
Water	49·2 c.c.
Sulphuric acid, 1·840	262·5 c.c.

The acids and water are mixed in the order named, and when a steady temperature of 70° is obtained the gelatinised cotton is immersed in it for twenty minutes. With some cotton the amount of water given above is inadmissible, as it immediately dissolves. The proportions of acids should be kept, and the water diminished to such a degree that the solvent action is reduced. After washing and drying, the

resulting pyroxyline will be found to have lost considerably in weight, and it should be almost powdery in appearance, and readily disintegrable. It will be found highly soluble in a mixture of ether and alcohol, and as much as 2 per cent. may be required to give a sufficient body to the collodion.

Hitherto cotton has alone been mentioned as capable of forming pyroxyline; but it may be stated that every analogous substance may be similarly treated. Thus linen and paper are amenable to the above treatment, and for some purposes they give superior results; for instance, Whatman's drawing paper has been found by Warnerke to give better results than the gelatinised cotton in the last process. Being already sized with gelatine, there is no need for the preliminary treatment pointed out.

The action of the solvents employed in the collodion on the pyroxyline deserves a passing remark, as many modifications in the resulting film can be caused by judiciously varying their proportions. The specific gravity of the alcohol employed should invariably be ascertained, as the condition of the sensitiveness of the plate depends much upon its strength. With a collodion made at a low temperature, the presence of a certain percentage of water is advisable, as its horny nature is thereby modified, and a certain degree of porosity obtained. A specific gravity of ·820 is in this case admissible. With the pyroxyline such as that obtained by the last formula, the water should be a minimum, as it is already porous, and the presence of water is apt to make it reticulated and rotten. The specific gravity in this case should rarely be over ·812. An excess of alcohol also tends to give porosity, and therefore sensitiveness; but if the addition be carried to an extreme, the very porosity diminishes sensitiveness, as the sensitive salts formed in the film coagulate into too large particles. Alcohol also diminishes the rapidity of setting. Ether, on the other hand, tends to close the pores of the film, as is demonstrated by coating a plate made with an excess of it, when it will be

found that a contraction takes place, causing the film to leave the edges of the plate, or to split on drying. The ether employed should be as pure as possible (this is not insisted on by manufacturers of collodion), as otherwise it is apt to liberate the halogen from the dissolved salts, giving rise to an alkaline reaction which is one cause of rottenness in the film, and an apparent want of body in collodion.[1]

The following are collodions for different processes.

For the wet process:

No. 1.	Pyroxyline, Hardwich's formula . .	12 to 14 grammes
	Alcohol, ·820	450 c.c.
	Ether, ·725	550 c.c.
No. 2.	Pyroxyline, Hardwich's formula . .	12 to 14 grammes
	Alcohol, ·820	500 c.c.
	Ether, ·725	500 c.c.

No. 1 is most suitable for cold, and No. 2 for warm weather.

For dry processes with the bath:

No. 3.	Pyroxyline, first formula	10 to 12 grammes
	Pyroxyline, last formula	4 grammes
	Alcohol, ·813 or ·814	500 c.c.
	Ether, ·725	500 c.c.
	Water	Quant. suff.

The water is shown in No. 3 to remind the student it puts a power into his hand of modifying the collodion in structure by its addition. It frequently happens that No. 1 or 2 formula may also be improved for dry processes by attending to the amount of water present.

The next point to be determined is the amount of bromide and iodide to be dissolved in the collodion, and to determine their proportions it will be well to enter into

[1] The student would do well to try the experiment of adding a small quantity of caustic potash to a phial of collodion, and noting the action that takes place.

detail as to their behaviour when converted into the silver compounds and exposed to the light. Iodide of silver in a film is capable of forming a dense image with a short exposure, but the gradations in density are often wanting when the light is extremely bright; added to which, if organic matter be present with it, even such as is to be found in many collodions, the picture is apt to be veiled and wanting in vigour.

Bromide of silver, on the other hand, is especially adapted for those collodions which have an organic reaction. It has usually been accepted that the iodide is the more sensitive of the two salts, but recent investigations tend to show that the bromide has the advantage, both as regards sensitiveness and delicacy, when developed by method 3 (p. 19). The failure of the bromide when developed by method 2 (p. 19), which is wet-plate development, consists in its comparative insensitiveness to very faint light as found in deep shadows. A bromo-iodide of silver, however, combines the advantages of the bromide with that of the iodide; for the wet process and certain of the dry processes it possesses every essential quality for the production of a good picture. The proportions of bromine and iodine in combination vary considerably, from 1 part of the former to 10 parts of the latter (which is just sufficient to secure cleanliness and freedom from veil with all ordinary preparations of collodion and bath) to 25 parts to 1. The latter proportion is never employed except in dry-plate processes. The iodide is usually fixed at about from 6 to 10 grammes per litre. The sensitiveness of the surface in all cases depends on the mode of development employed. Thus for a wet plate, Vogel has found that the proportion of iodine to bromine should be about 4 to 1 to secure the greatest sensitiveness, whilst with the alkaline method it is diminished to the smaller proportion, or it may be omitted altogether when a dry process is in question. At present we

are considering the wet process, and not the more modern dry processes where the conditions are different. The metal with which the iodine and bromine are combined when introduced into the collodion serves to exercise a great influence on the sensitiveness of the surface. Some years ago Warnerke stated that the metals combine with the pyroxyline and form compounds whose composition is as yet undetermined, and thus the difference in structural effect and viscosity exhibited between two identically similar collodions when iodised with a cadmium and an alkaline salt may be accounted for in a great measure. For experiment, it will be advantageous if the student iodise two portions of collodion; one with 4 grains of cadmium iodide, and the other with 4 grains of potassium iodide, and note the difference in their behaviour when poured on a plate. With the latter he will find a freely flowing fluid; with the former, one which is more glutinous, and difficult to manipulate.

It also appears that the different metallic salts in solution cause different degrees of sensitiveness in a film. This has been investigated by Warnerke, who places them in the following order for imparting sensitiveness and intensity:

Order of sensitiveness . . .	Zn	Cd	Na	Fe	NH_4	K	U
Order of intensity of image .	Zn	U	NH_4	Cd	Na	K	Fe

The alkaline iodides are those which are most prone to decompose under the action of ether, particularly if it be methylated; hence, for a collodion to keep long, it is necessary that the purest form be employed. As before shown, when the iodide is decomposed, the alkali decomposes the pyroxyline, rendering it very fluid and defective in setting qualities, whilst the iodine itself increases the density of the image, probably by the formation of a silver iodate.

In bromised collodion it is very rare for bromine to be set free, and in bromo-iodised collodion the dark colour

obtained by long keeping is invariably due to the iodine liberated, for *uncombined* bromine will always displace iodine. To increase the density of a developed image it is always advisable to add a little tincture of iodine to a collodion.

In choosing the iodide or bromide of any particular metal for iodising or bromising a collodion, it must be remembered that it is the amount of iodine and bromine that are the essentials, and not the metal. Hence, 4 grains of ammonium iodide and 4 grains of cadmium iodide mean a totally different quantity of iodine. The amounts may be calculated from the combining weights given.

The following formulæ will be found to give collodion suitable for the ordinary wet process:

No. 1.	Ammonium iodide	7 grammes
	Cadmium bromide	4 grammes
	Plain collodion [1]	1 litre
No. 2.	Ammonium iodide	8 grammes
	Cadmium bromide	2·5 grammes
	Plain collodion	1 litre
No. 3.	Cadmium iodide	9 grammes
	Cadmium bromide	4 grammes
	Plain collodion	1 litre

Nos. 1 and 2 are speedily ripe enough for use; with a little alcoholic tincture of iodine added they may be employed immediately.

No. 3 requires keeping, as at first it will not flow freely. A sample of collodion such as No. 3 has been kept two years without deterioration, the precaution being taken to keep it in the dark and in a cool place.

No. 2 is suitable for dry-plate work and for interiors, but as a staple article No. 1 is recommended.

[1] It must be borne in mind that the collodion may be made by 1, 2, or 3 formula, and the pyroxyline may be of the varying types shown at p. 135. Formula No. 2 is that usually to be recommended.

For a simple iodised collodion the following formula may be adopted :

No. 4.	Ammonium iodide	8 grammes
	Plain collodion	1 litre

or,

No. 5.	Cadmium iodide	10 grammes
	Plain collodion	1 litre

No. 4 should be used immediately after making, whilst No. 5 will keep almost indefinitely.

The next formula is for a simple bromised collodion :

No. 6.	Zinc bromide	16 grammes
	Plain collodion	1 litre

For all the above iodides and bromide substitution may be made with others, and it by no means follows that those chosen as examples will prove the most sensitive, though experience has shown they give good results. It is customary in preparing plain collodion to omit half of the alcohol, and to employ that half as a solvent for the haloid salts. This is convenient but not absolutely necessary. It is a good plan to make a note of the date of the manufacture of the collodion, as also of its iodising ; useful information is often given by such memoranda.

Testing Plain Collodions

Plain collodion should be tested before iodising, and the following tests may be applied, recollecting that a film that may not be suitable for the bath process may still be suitable for an emulsion process, and *vice versa*.

Coat a plate (in the manner described at p. 149), and ascertain if when dry the film is dead white, opalescent, or transparent. If the first, it is unsuitable for any process ; if the second, it may be employed for emulsion work ; whilst if the third, it may be suitable for any process.

Coat a plate, and, after the collodion has set, mark if it

is powdery to the touch, or if on applying the finger it comes away in strips. If the former, it may be good for dry-plate work ; if the latter, for both dry plates or the wet process.

Coat another plate, and, after setting, wash the film under the tap till all the solvents are washed out, and note if it take an even film of water or if it repels it at parts. If the latter it is too horny to use in the bath processes; a little potassium carbonate may improve it.

Note if the collodion flows freely, viscously, or lumpily. Too limpid a collodion will fail to give density ; too viscous a collodion is unsuitable for any but small plates, whilst a lumpy collodion will give irregular images. The flowing qualities of a collodion arising from the pyroxyline may often be corrected by altering the proportions of ether and alcohol.

If the film be reticulated, having marks like a crape pattern on it, the solvents may not be sufficiently anhydrous, or the pyroxyline may be in fault, as before stated.

The collodion should also be tested after iodising ; the defects will be noticed when treating of the defects in negatives produced by the various processes.

CHAPTER XV

COLLODION PROCESSES

THE plate, before being taken into use, should be most carefully cleansed from dirt of any description. The success of a photographer may be said to depend in a great measure on the effectual manner in which he completes this operation. The dirt that is to be looked for on a glass plate is that due to the manufacture, that due to subsequent exposure to the atmosphere and to the hands of the packers, and sometimes that due to the chemical compounds with

which it may have been in contact. Ordinary plates are sometimes found to be gritty on what should be the polished surface, and the application of acid may dissolve the grits away. Hence it is a good plan to treat all new plates with a solution of dilute nitric acid (10 parts of water to 1 of acid). This will not rid them of mechanical dirt, such as dust or grease. The presence of dust is readily accounted for, but the origin of the greasy matter is far more difficult to understand. If a plate that is thoroughly cleaned be put away in a plate box for a few days, and be then examined by breathing on it, it will be found that it shows signs of repelling the aqueous vapour from the breath in certain parts, and that a subsequent cleaning of the plate is necessary to render it fit for use. This phenomenon can be accounted for on the supposition that organic matter of a fatty nature is to be found in the atmosphere, and when we remember that the lungs expire not only carbon dioxide, but also various organic matters, we should expect that in an inhabited house this latter might condense on some dry cool surface. The danger of using plates on which this deposit exists will be apparent by a simple experiment. Rub a warm finger or hand over the plate, coat with collodion, sensitise, but do not expose to light; then apply the developing solution and watch the result. It will be found that where the contact has been made a reduction of metallic silver will take place, and as development proceeds a dark stain will be produced. Imagine a similarly treated plate, prepared as before, exposed in the camera and developed; a dark deposit will take place both where the hand has touched and also where the invisible image has been impressed. It may be said that all animal organic matter has the property of causing a tendency for metallic silver to be reduced from the solutions of its salts. A similar remark applies to the mercury compounds which sometimes get invisibly reduced in the surface of the glass. The composition of dust is of a most varied nature, and not unfrequently

consists of ferric oxide, sodium chloride, and other earthy constituents. The reduction of silver nitrate in the presence of some of these would be certain.

Alkalis have the property of converting greasy into saponaceous matter, and spirits of wine will dissolve both soap and grease; hence both are employed as detergents. Mechanical dirt requires friction to remove it, and this should be just sufficient for the purpose, yet not enough to injure the surface of the glass. Such bodies we have in tripoli powder and rouge. The former is recommended on account of its being less gritty than the latter. The most common cleaning solution is made as follows:

Spirits of wine	50 c.c.
Tripoli powder: Quantity sufficient to make a thin cream	
Ammonium hydrate	1 c.c.

Mr. Warren De la Rue for his astronomical photography employed a solution of potassium dichromate and sulphuric acid. This is doubtless a most effective detergent, but the use of sulphuric acid is open to objection on account of the damage it may do to the dress or hands.

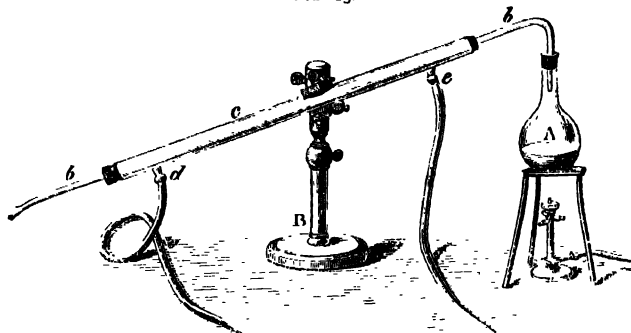
The writer has heard of a process of cleaning recommended in which it was proposed to employ potassium cyanide, followed by nitric acid. The student is earnestly recommended not to attempt this plan, as it is poisonous and highly dangerous.

Boiling the glass plate in caustic soda or potash has also been proposed. This is apt to injure the surface of the plate, owing to the slight solubility of vitreous matter in solutions of the caustic alkalis. Perhaps no more effective method for securing a clean plate can be adopted than by first treating the plate with a cold solution of caustic potash, rubbing it well in with a rag, and then immersing it in dilute nitric acid and washing under the tap. A final thorough rinse in distilled water, and a rapid drying in a water-oven, will leave the plate in as clean a state as can be desired.

Sensitising Bath.

The sensitising solution—that is, the solution in which the collodion containing the soluble iodides or bromides, or both, are immersed in order to form the iodide bromide, or bromo-iodide of silver— may be said to be invariably made of silver nitrate dissolved in water. The purity of both constituents is of the highest importance, as any extraneous matter may be fatal to obtaining good results in development. Distilled water is naturally the purest form of water that can be obtained, but even this is sometimes contaminated with organic matter in solution, which is apt to react

Fig. 23.



upon the sensitive salt. The manner in which ammonia is carried over with the aqueous vapour is well known to any chemist, and in a similar way hydrogen sulphide can be carried over. The latter contamination is most hurtful to sensitiveness, and the former might cause fog. It may be useful to point out the best mode of distilling water in a small way, in order to obtain absolute purity.

A glass retort is always clean, and dirt can be more readily seen than if it be of metal. The form known as Liebig's condenser is therefore recommended instead of the ordinary still. The water should be placed to the level of the flask A shown in the diagram, and a little (say a gramme

to a litre) caustic potash should be dissolved in it. This will free the water of any ammoniacal compounds when warmed. The distillation takes place through the glass tube, *b*, round which is placed a glass jacket, *c*, containing water. Cold water is allowed to enter the jacket by the tube, *d*, and the heated water is carried off by *e*; a universal clamp, B, is useful for holding the condensing apparatus in position.

The first 50 c.c. of each litre distilled should be rejected, and the distillation should not be continued beyond that point where 100 c.c. are left in the retort. The distillate may then be considered to be pure enough for photographic purposes. If an ordinary worm still be employed, care should be taken that the worm is clean, free from dust, and not of lead. The water should be distilled over as before, the first and last portions being rejected. If distilled water cannot be obtained for making up the solution, spring water, if not impregnated with sulphates, will generally answer. Failing these, river water, and lastly rain water, after twice filtering through charcoal, must be resorted to. At first it may seem strange to place rain water last on the list, but it should be remembered that it is almost invariably collected from the roofs of houses, and is consequently sure to be contaminated with organic matter, and also inorganic matter. Rain water, if it could be collected directly as it falls, would save the necessity for using distilled water. A method of purifying ordinary water for bath purposes is as follows: Boil and filter it, add a little barium nitrate to it, and see if it turns milky. If such be the case, add a small further quantity, together with a few crystals of silver nitrate to each litre of water, and place in the sunlight. After a few hours' exposure, the organic matter and sulphates will be at the bottom of the containing vessel, and the supernatant water may be decanted, syphoned, or filtered off. An excess of barium nitrate is not hurtful to the solution, for, as will be seen at p. 147, its addition is recommended.

Nitrate of silver should be pure. The uncrystallised will be found sufficiently free from nitric acid to be available for forming a bath solution needing no doctoring. It is sometimes adulterated ; if any suspicion of this arise, a certain known quantity of the crystals should be dissolved up in water, and the amount of silver nitrate really present calculated by any of the methods usually adopted. Silver nitrate is readily soluble in its own weight of water, but this strength would be quite unsuitable for a sensitising solution for two reasons : first, silver iodide is soluble to a certain extent in silver nitrate solution. The stronger the latter, the greater the amount of iodide dissolved. A variation in temperature also affects the quantity capable of being held in solution. Now, even supposing that at the temperature at which the bath was formed immersion of an iodised plate took place, the heat evolved in the act of combination between the soluble iodide and the silver nitrate to form the sensitive compound would be sufficient to cause the iodide in the film to be partially dissolved out. Secondly, the formation of the iodide would be so rapid that there would be a coarseness in the particles unsuitable for rapidity. Sutton has demonstrated that where any iodide is in the solution, 10 per cent. is as great a strength as can well be managed, whilst a 5 per cent. solution is the limit in the other direction. When bromides alone are employed, the strength may be 15 per cent., as the silver bromide is almost insoluble in silver nitrate solution.

In preparing a bath it is generally saturated with silver iodide, to prevent the silver nitrate dissolving away portions of the sensitive surface. Some skilled photographers, however, prefer the saturation to take place from the film itself, a method which is recommended to the student, if he exercise ordinary care in working his plate. The degree of acidity of the bath depends much on the iodising or bromising of the collodion. To secure the greatest degree of sensitiveness, if iodide alone be present the solution

should only be faintly acid, with bromo-iodide it should be distinctly acid, whilst with bromides alone it should be very acid. The rationale of the different degrees of acidity is as yet not known accurately, more investigation into the subject being required; but it may be presumed that it is in a measure dependent on the behaviour of the silver bromide and iodide when exposed in the presence of silver nitrate.

The following formula for the silver-bath solution is a standard one where iodide or bromo-iodide of silver is the sensitive salt to be produced:

Recrystallised silver nitrate . .	80 grammes
Water	1 litre
Potassium iodide	·25 gramme

The silver salt should be dissolved in a quarter of the water, and the potassium iodide added to it after solution in the least possible quantity of water. After shaking (which will cause a partial solution of the silver iodide first formed), the remaining water should be added, when a further emulsion of iodide will appear. When filtered out, the bath solution will be ready for use, supposing proper acidity to be attained.

An excess of acidity may be corrected by the addition of a few drops of a sodium carbonate solution. When a permanent precipitate is obtained, the requisite acidity should be given *after filtering* by adding a few drops of a 5 per cent. solution of nitric acid. Some photographers have recommended the employment of acetic acid instead of nitric acid, but the writer has never found any benefit resulting from it—in fact the reverse; for although acetic acid added to silver nitrate will not at first form silver acetate, yet as the solution becomes contaminated by working there is danger of compounds forming, which will combine with it, and finally cause decomposition between the new compound and the silver salt.

As the bath solution gets worked, that is, has many plates immersed in it, the original purity becomes impaired by the accession of ether, alcohol, and various nitrates from the collodion, besides any extraneous matter that may accidentally be carried in. After a time the vigour and cleanliness of the developed image will be found to diminish, and the strength &c. of the bath has to be attended to. Gently warming it will get rid of the ether, and evaporating it to half its bulk will get rid of most of the alcohol. If organic matter be present, exposure of the bath (after neutralisation of the free acid with sodium carbonate) will cause metallic silver to be precipitated, and itself to be oxidised by the liberated molecule of nitric acid, thus rendering it innocuous.

With certain collodions acetic acid will find its way into the bath, and the best method of eliminating the silver acetates which will probably have been formed is to evaporate the bath to dryness and add some strong nitric acid. This will liberate the acetic acid, which may be driven off by a further application of heat. None of these modes of treatment will eliminate all the impurities, for all the foreign nitrates (except ammonium) remain almost unchanged, even by prolonged fusion; nothing remains but to precipitate the silver as chloride, or in the metallic state. If a film, after withdrawal from the bath, presents an appearance as if fine particles of the sensitive salt had been sprinkled over it, the solution is 'over-iodised'; that is, it is supersaturated with silver iodide. The disturbance made by the immersion of the plate probably causes the deposit. Diluting to double its bulk, next filtering, and then making up the solution to proper strength, will be a cure, or, as some photographers aver, the addition of 2 per cent. of barium nitrate will answer the same end.

CHAPTER XVI

MANIPULATIONS IN WET-PLATE PHOTOGRAPHY

Cleaning the Plate

THE glass plate must first be cleaned with one of the detergents indicated in the last chapter. If the tripoli powder cream be employed, it should be applied with a small pledget of cotton wool or soft rag, taking care that both sides of the plate are covered with it. It may either be allowed to dry on the plate, or, whilst still wet with the alcohol, may be wiped off with a soft diaper duster. In the latter case a little practice is required to prevent markings on the plate as shown by breathing on it. When the tripoli powder is all rubbed off, a final polish should be given to both surfaces with a chamois leather or old silk handkerchief.[1] The polishing should be such as is used in French-polishing a table; not too heavy a pressure should be exercised, and there should be a continuous circular motion. It should be remembered that the effect of rubbing silk on glass is to generate electricity, which is sometimes a cause of non-adherence of the collodion to plates. The electricity in the glass should be allowed, or caused, to be dissipated before collodion is applied. There are various appliances for holding plates during cleaning, some of which are excellent in their way, whilst others are toys made on principles unmechanical. They are not necessary for the size of plate with which an amateur is likely to work.

If a plate be clean the moisture from the breath will leave it evenly. It must be freed from dust before collodionising, by passing a badger-hair brush over its surface.

[1] Before taking these into use, they should be thoroughly cleaned from all greasy matter by washing with soda.

Coating the Plate with Collodion

The plate may be held in its centre by a pneumatic holder such as that in fig. 25, or at the corner by the fingers, if care be taken that no portion except the edges are touched. From a half-filled 6-ounce bottle, or from what is known as a collodion pourer (fig. 24), the collodion should be carefully poured upon the plate, so as to form a circular pool at the end farthest away from the manipulator, and gradually be allowed to cover the entire surface, the wave flowing from the right-hand to the left-hand top corner, from thence to the left-hand and right-hand bottom corners, and finally into a stock bottle, whence, after decantation, and (if necessary) dilution with 2 parts ether to 1 of alcohol, it can be again employed. When the collodion is thus poured off, the plate will be in nearly a vertical position, and a gentle rocking motion should be given to it to prevent the collodion setting in ridges; but the precaution should be taken not to grind the edges against the bottle, otherwise particles of glass may appear on subsequent plates. In hot weather the collodion does not take so long to set as in cold. The state of the film can be always ascertained by cautiously touching the left-hand bottom corner with the finger. When no longer tacky, the plate is ready for immersion in the bath. The collodion should be filtered if necessary, or it may be decanted from a stock bottle by one of the ordinary syphon arrangements.

FIG. 24.

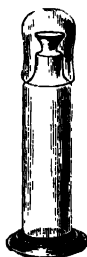
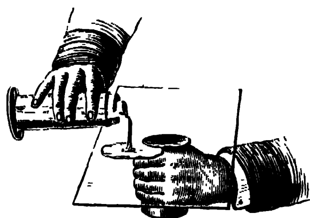


FIG. 25.



Sensitising the Plates

The film of collodion having set, the plate is immersed in the sensitising solution contained in a vertical or horizontal bath, the former being recommended for small plates, though the latter is essential for large sizes. A 'travelling bath' is perhaps the best form of bath holder, as it is useful for indoor and also for outdoor work. It is of the form given in the figure. The top of the glass solution-holder, B, which is held in a case, A, is closed by a water-tight india-rubber top, D, screwed down by the screws C as shown. The 'dipper' employed for carrying the plate into the solution during the operation of sensitising

FIG. 26.

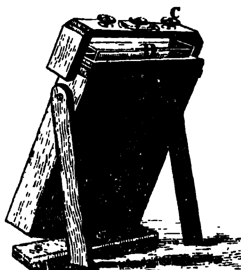


FIG. 27.

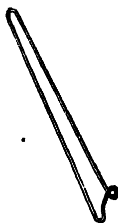


FIG. 28.

may be conveniently made of PURE silver wire, of the shape indicated in fig. 27. It is usually, however, made of ebonite or glass (see fig. 28). When the plate is covered with the solution by a steady downward motion of the dipper into the bath, it is moved slightly up and down in the fluid to wash off the ether from the surface of the film, and when all

greasy appearance has vanished, it may be left quietly at rest for from one to five or six minutes, according to the temperature and amount of bromide[1] present. The motion of the plate in the bath at first is important; as, if neglected, streaky negatives are apt to result, especially in summer weather.

It need scarcely be said that the silver nitrate solution should be free from all sediment before a plate is immersed in it, and it should be kept in order as shown at p. 147. After being *very slowly* withdrawn from the bath, capillary attraction will be exercised by the solution in the bath on that left on the film, and there will be but a slight quantity left on the plate, quite insufficient to cause the necessity of long draining. On the other hand, quick withdrawal necessitates long draining on a pad of blotting-paper; the edge that occupied the lowest position in the bath should be pressed against it. When the surface appears free from excess of moisture, the plate is placed in the dark slide, taking care that the edge that is to occupy the top place in the camera is kept in the same relative position. The slide is closed after the back of the plate has been dried with a piece of rag or blotting-paper. It is here presumed that the camera is in position, and that the view has been focussed, following out the rules given in chap. xxiii., p. 294, and that the exposure is given also in accordance with the remarks to be found on p. 313.

The following are the formulæ usually employed in development:

No. 1.	Pyrogallic acid	1 gramme
	Glacial acetic acid	20 c.c.
	Alcohol.	Quant. suf.
	Water	500 c.c.

This developing solution is usually employed for simply iodised collodion, and is useful when great density in the

[1] The greater the amount of soluble bromide in the collodion the longer it takes to sensitise fully.

lights is required. The iron developers of a weak and strong type are as follows :

No. 2.	Ferrous sulphate	10 grammes
	Glacial acetic acid	30 to 40 c.c.
	Alcohol.	Quant. suf.
	Water	1 litre
No. 3.	Ferrous sulphate	100 grammes
	Glacial acetic acid	40 c.c.
	Alcohol.	Quant. suf.
	Water	1 litre

These formulæ give the limiting proportions of ferrous sulphate to water admissible, but any quantity between the two may be taken. For ordinary work, about 40 grammes is usually taken, as giving the best results. The double sulphate of ammonium and iron may also be substituted for the ferrous sulphate, and it has the advantage of remaining in solution unchanged for a long period.

The addition of copper sulphate to an extent equal to half the quantity of ferrous sulphate employed is also recommended by some operators, and it has doubtless in some cases a beneficial effect.

The addition of various colloidal substances to the developers, as already stated, may sometimes be desirable, particularly where great density and fine deposit are requisite. Perhaps the best of any is that proposed by Mr. Carey Lea. It is made as follows: 30 grammes of French glue, or gelatine, is softened in 50 c.c. of water, to which 3½ c.c. of sulphuric acid is added. The water is next boiled, and the gelatine dissolves, and, after adding another 10 c.c. of water, the boiling is continued for a couple of hours. Five grammes of metallic zinc are next added, and the boiling continued one hour and a half longer. The solution is allowed to settle, and the clear liquid decanted off. To every 3 grammes of ferrous sulphate, 1 to 2 drops of this solution suffices to give sufficient restraint, without the addition of any acetic or other acid.

Ferrous sulphate is a very unstable body, and will absorb oxygen from the air, and speedily attain the ferric state; and as the latter salt is incapable of absorbing more oxygen, it is evident that the developing qualities are thus annihilated. It has been in effect found that ferric sulphate is a retarder, that is, a body which prevents the rapid deposition of the metallic silver from the nitrate solution. The lesson to be learnt from this is, that when the developer attains a red colour it must of necessity be slower in action than when of the ordinary apple-green tint. A simple experiment with a developer containing ferric sulphate is worthy of trial by the student. Take, say 3 grammes of ferrous sulphate, and having dissolved it in 50 c.c. of water, boil with strong nitric acid to such an extent that the addition of a drop of the solution to one of potassium ferricyanide produces no blue precipitate. Next precipitate the iron as ferric oxide by ammonia, filter, wash well, and dissolve up in the least possible quantity of sulphuric acid, taking care to leave a slight residue undissolved. Make up the quantity of liquid to 10 c.c., and add 2 c.c. to a solution of ferrous sulphate made according to formula No. 3, omitting the glacial acetic acid. Develop a picture with it, and note the result.

Attention should be paid in all cases to the crystals of ferrous sulphate employed. They are frequently mixed with a yellowish powder, due to the decomposition of the salt. In common specimens this often bears a considerable proportion to the ferrous salt itself, and must be allowed for in making up the solutions. The strength of the acetic acid is also important. What is commonly sold as glacial is often below strength. Its value should be estimated as given in various works on chemistry. In warm weather, owing to the increased rapidity of chemical action, more acetic acid is required to control the reduction of the silver nitrate. Hence these quantities shown may require modification according to the temperature.

The amount of alcohol required is invariably shown as

'quant. suf.' No definite quantity could be given, as it varies according to the amount of alcohol present in the bath solution. With a new bath none at all is required, whilst with one in which a large number of plates have been sensitised as much as 40 c.c. to the litre may be necessary. A deficiency or excess of the alcohol is shown by the solution refusing to flow evenly over the surface of the sensitised collodion, and running into rivulets and tears. This is caused by the difference in surface tension of the fluid on the plate and the developer. Any body which reduces the deficiency may take the place of the alcohol. Thus a more viscid solution, such as that given by the gelatine retarder, is effective, no alcohol being required with it, even when the bath is very old. Methylated alcohol[1] should be avoided as far as possible, stains and disfigurements in the developed image being often attributable to it.

Development

Having decided which developer is to be employed, making the decision after a careful study of the picture, and noting its peculiarities, the plate is removed from the dark slide, the same precaution of keeping uppermost the edge which occupied the top in the camera being taken as before. If this were neglected the bath solution which might have accumulated at the bottom edge might flow back over the surface, and thus inevitably cause irregular development if nothing worse. The developing solution having been placed in a clean cup, it is swept with an even motion, without being allowed to stop, over the plate, which is held by a pneumatic holder, or by the fingers, as in coating it with collodion. Little or none of the solution should be allowed to leave the film, unless it be feared that too much density will be

[1] Spirits of wine, sold as methylated, sometimes contains a certain quantity of resinous substance and mineral oil, in order to satisfy the excise requirements.

given to the resulting image, in which case it is an advantage to let it wash off a portion of silver nitrate. As the picture appears, the developer is caused to work round to every corner in succession, thus securing an evenness which would otherwise be wanting. An over-exposed picture will flash out at once, and, unless the plate be immediately washed, a veil or fog will inevitably be deposited on the surface, caused by the too rapid reduction of the first particles of silver, and the consequently rapid reduction of the remainder. An under-exposed picture will develop very slowly, and will always be wanting in detail by transmitted light, though it may appear fully out when looked at by reflected light, if held over a black background such as the coat-sleeve.

A properly exposed picture should develop gradually and evenly, and should take at least half a minute in warm weather to come fully out in every part. When no further action is manifest, the developing solution should be thoroughly washed away, and the next operation should be proceeded with.

Intensifying the Negative

This operation is one in which great judgment is required by the manipulator. Too great an opacity will spoil the negative, giving a black and white picture when printed; whilst, on the other hand, one not sufficiently opaque will yield a grey print, which is unsatisfactory. The opacity must be judged of by the *colour* of the deposit as well as by the *density*, though the former need not be taken into account when the iron developer has been used, as the silver deposit caused by it is of a blackish grey. If a pyrogallic acid developer be employed the colour is of a decidedly reddish tint, and proportionally non-actinic; hence great judgment is necessary to ensure a really good result. When intensity is procured by using the pyrogallic solution the same remarks hold good, though the colour is never so

marked as when arising from development. Whatever course be decided upon, it should be borne in mind that the general character of the finished negative will always bear an exact relation to that given by the primary development. Thus a flat-looking developed image will yield a flat-looking picture, whilst one full of gradation will yield one similarly graduated.

Should intensification be necessary, the operator must determine whether it would be more advantageous to conduct it before fixing the image, or afterwards. Should over-exposure have been given the latter will be advisable, whilst, if undue exposure, it should certainly take place before fixing. The intensifier should be poured over the plate, and, whilst so remaining, a few drops of the silver nitrate solution should be dropped into the cup, and then the intensifier poured back. The solution is again swept over the plate, and the required density is obtained by deposition of the silver.

It has been a point causing some discussion as to whether a developed picture may see light before being intensified. The answer to this seems simple. With an iodised film, which has been well washed after development, it may be exposed to tolerably bright light without any danger of producing a veil by the action of the intensifier, since silver iodide is almost insensitive to light, except in the presence of an iodine absorbent. With a bromo-iodised film more caution is required, though the writer has never found that a short exposure in a moderately strong light is hurtful. With a bromised film the less exposure given between the two operations the better.

When intensifying after fixing, it is customary to flow a little iodine over the film, then to expose it to light, and afterwards to use the pyrogallic solution. This is nearly useless unless a little free silver nitrate be present, or all excess of iodine be washed out, any trace of which would render the exposure inoperative. The writer recommends a

little bromine water instead of the iodine, for reasons which will be apparent on reading the chapter on emulsions.

In intensifying after fixing, there is a danger of staining the shadows with a reddish stain. This seems to be more due to a pyrogallic stain than to deposited silver, and can usually be got rid of by a little acetic acid diluted with an equal bulk of water.

For landscape or portrait negatives it is seldom wise to resort to any method of intensification, except that with silver, as there is great risk of making the half-tones too opaque. The iodide of mercury formula is perhaps the best, if anything more be necessary.

Fixing the Negative

This operation calls for little remark. The plate may be immersed in a vertical or horizontal bath if the sodium hypo-

Fig. 29.

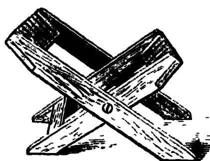
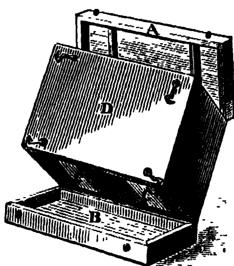


Fig. 30.



sulphite solution be employed, or it may be applied by flowing it over the plate: this should always be done with the cyanide solution. Attention should be paid to see that all the iodide, bromide, or both be dissolved away. This can be ascertained by reversing the plate and noting if the yellowish-green colour due to them be absent. Finally the plates should be well washed and drained. A neat contrivance for holding the plates when drained is

shown in fig. 29. As it folds up it is suitable for field work, though a draining box is usually carried, made as in fig. 30.

Varnishing the Negative

The plate may be allowed to dry spontaneously or by the aid of heat ; the latter method gives a slightly denser image, and therefore a negative should never be heated when parts of it are dried by ordinary evaporation. Before applying the varnish the plate must be warmed, to cause the varnish to flow, and also to prevent it drying matt. The varnish is applied like collodion, the same procedure being followed exactly. When all that will has run back into the bottle, any excess that may have collected at the corner end may be removed by pressing the glass on a pad of blotting-paper. The plate must again be warmed.

The sources of heat are various. In India, or in other hot climates it will be found that exposure to the sun's rays imparts sufficient warmth to the glass. In temperate climates the neatest way of attaining the proper temperature is by placing the plate in a water oven, as used in chemical operations (see fig. 37) ; failing which, a clear fire, a Bunsen rose burner, or a paraffin lamp may be brought into requisition. A naked spirit-lamp is dangerous without great care, and the solvents of the varnish, being highly inflammable, readily catch fire from any naked flame.

Defects in Negatives

A mere mention of some of the defects that are to be met with in negatives will suggest a cure, whilst for others, which are a little recondite, explanations will be offered and remedies suggested.

'Fog' on a negative may be due to several causes : 1, it may be due to a dirty plate ; 2, to over-exposure ; 3, to an alkaline bath solution ; 4, to want of acid in the developer ; 5, to improper exposure to actinic light, either in the camera

or in the dark room; 6, to vapour in the developing room or tent. A minute examination of the condition of the negative and the state of the dark room or tent will generally show the cause of the defect, which has only to be known to be rectified.

A weak image may be due—1, to an unsuitable collodion, a weak sensitising bath; 2, a bath charged with organic matter; 3, bad lighting of the subject due to dull weather or a yellow light; or, 4, an over-strong developer.

Pinholes in the negative may be caused by—1, dust on the plate; 2, the bath being over- or under-iodised.

Black specks on the picture are usually due to—1, dust in the camera; 2, slide; 3, dark room; or, 4, dust in the collodion.

Comet-like spots are almost always due to undissolved particles of pyroxyline in the collodion.

Transparent spots, as distinguished from pinholes, are usually due to dust in the collodion.

A scum on the film is usually found when a plate has been kept for a long period out of the bath, or when a too strong development has been used. A plate which is to be kept for a long time before development should be sensitised (or finally dipped) in a weak bath, and only immersed in it sufficiently long to cause all repulsion between the surface of the plate and the solution to be overcome. A collodion containing a larger than usual proportion of bromide is also recommended to secure freedom from stains.

The usual explanations given as to the cause of markings like watered silk, are that the collodion contains too much iodide, is too alcoholic, or that the pyroxyline is too strong. The remedies have already been indicated. Black stains at the corners of the plate are often caused by the bath solution flowing back over the sensitised surface, after having been in contact with the wood of the dark slide.

Transparent markings are much more common in cold

than in hot weather. They generally arise from unequal sensitising of the film in the bath, and from the developer refusing to flow.

CHAPTER XVII

DRY-PLATE PROCESSES WITH THE BATH

It is not proposed to enter into details of many dry-plate processes with the silver bath, as they can be ascertained by the consultation of various manuals. At the same time it is thought advisable to enter more fully than usual into the theory of the subject. The course usually adopted for these processes is as follows:

The plate is coated with a preliminary substratum of gelatine, albumen, or india-rubber, or else is given an edging with one of them. The collodion is then applied, and sensitising takes place in the usual manner. The silver nitrate solution is next thoroughly washed off in distilled or rain water, and what is known as a preservative is flowed over the surface of the plate. The preservative may be partially washed off, or it may be allowed to dry on it in undiminished strength. The plate is now in a state ready for exposure.

The preliminary coating or edging of albumen is given to the plate in order to secure the adhesion of the collodion film. It is found in practice, if this be omitted, that the film, on being wetted, becomes non-adherent, and floats off. The substratum, as it is technically called, must always be of such a nature as not to injure the bath solution, and, to guard against all risk, it is advisable that every portion of it should be covered with collodion. The following are formulæ for it:

Albumen	1 part
Water	50 to 100 parts
Ammonium hydrate:	Sufficient to give it a smell of ammonia.

or

Sheet gelatine	3 grammes
Ammonium hydrate	15 c.c.
Water	1,500 c.c.

The gelatine should be soaked in half the quantity of water, and the remainder added boiling. When cool, the ammonium hydrate should be dropped into the fluid. This solution will not keep, hence it is advisable to make it up only just when wanted.

When it is required to cover the entire plate with either of these substrata, it is usual to wet the plate with distilled water, and flow it over, and drain. It frequently occurs, however, that this method produces markings on the negative. A simpler and more effective plan is to cover the end of a glass plate (the breadth of the plate to be covered) with a piece of fine flannel or swan's-down calico, to moisten it with the fluid, and then to squeeze out all excess. This brush, known as Blanchard's brush, is drawn down the plate with an even stroke; it gives the very finest coating possible. A washed and unpolished plate seems to take more kindly to the colloid body than if the cleaning be finished off with the silk handkerchief or chamois leather.

In lieu of either of the above solutions the following may be flowed over the plate like collodion, and be allowed to dry spontaneously:

India-rubber	1 gramme
Benzene	500 c.c.

The collodion should be of such a character as to give great density to the developed image. It should also give a porous film, for it must be remembered that when the pyroxyline parts with its water of hydration it becomes extremely impermeable to all solutions; so much so that a horny collodion will often refuse to develop. It has been the practice with many practical photographers to keep the iodised collodion till it is thoroughly aged, and has a ruby

tint from the elimination of iodine from the iodides of the alkalis, and the consequent combination between the alkali and the pyroxyline. This effect is precisely similar to that obtained by a modification of the ratio of the acids to the water in the manufacture of the pyroxyline. Collodion may also be rendered porous by adding water to a portion of it to such a degree that it gives a reticulated film, and by then adding the remainder unwatered. A slight opalescence of the film is not objectionable, and it may even dry almost matt, so long as the necessary disintegration of the pyroxyline is secured, since it is found that varnishing takes away the dead appearance to a great degree.

The sensitising bath should be such as to give a good dense film after the plate has been immersed some time. The solution employed for the wet negative process is of proper strength, unless the collodion be highly bromised, in which case the amount of the silver nitrate may be increased to half as much again, or even to twice the quantity.

After sensitising, it is usual to wash the plates to such an extent as to free them from all silver nitrate solution. The first washings are usually made in distilled or filtered water. Rain water is often recommended, but the operator should beware of it, unless it be very clean and at least be twice filtered. Perhaps more bad dry plates are produced by the use of impure washing water than by anything else. When the delicacy of the effect that is produced by the ethereal waves of light on the pure products is taken into consideration, it will be apparent that every extraneous force which will overthrow the equilibrium of the particles should be avoided. Thus we might expect that hydrogen sulphide might cause that overthrow, and it inevitably produces fog. A moderate proportion of iron in the water would also produce like results. When the first excess of the silver solution is washed away the danger of the use of impure water diminishes rapidly, and almost any *ordinarily* pure water may be brought into requisition, but in any case a final rinse

of distilled water is to be strongly recommended. Care should be taken that the surface of the plate after withdrawal from the bath is covered by the water without stoppage. The first washings may be well performed in a dish, and an even covering of the surface can be attained after a few attempts. Washing in distilled water should continue till all repellent action due to the alcohol and ether contained in the bath solution disappears.

Applying the Preservative

The preservative is usually applied by floating it on the surface of the film for about a minute. Care should be taken that its strength is not diminished by too much water being left on the plate. In some cases it may be applied by immersing the plate in a flat dish or dipping-bath containing it. There are some objections to this mode of application however.

It will be convenient here to discuss the ends to be obtained by the use of a preservative. 1. It must be an iodine or bromine absorbent, for without this quality the film manifestly might be insensitive. 2. It must be capable of filling up the minute pores of the collodion, so that on re-wetting after drying it may give access to the developing solution. 3. It must act as a protective varnish against the atmospheric influences. Regarding the first point there is not much difficulty, as nearly every organic animal or vegetable compound is capable of combining with iodine. Under the head of absorbents we may rank tannin, pyrogallol, gallic acid, gums, gelatine, albumen, caffeine, theine, and other like bodies. The second requirement may be met by the employment of some of the above, or by the addition to them of sugar in various forms. The last requirement is more difficult to meet, and is very often neglected, as it entails that the body should not be hygroscopic. The drawback to any processes, for instance, in which the preservatives contain gum arabic is that moisture is attracted, and the

sensitiveness of various parts of the plate is affected. No better varnish is known than albumen, though this has its disadvantages as regards rapidity, unless the greater proportion of it be removed previous to desiccation, or unless it itself becomes a vehicle for holding the sensitive salts, as in the collodio-albumen process. In the writer's opinion an unexceptionable preservative has yet to be found. It appears dubious whether it will not become advantageous to dispense with it altogether, when the balance between the pyroxyline and sensitive salts is properly adjusted, as in the case of emulsion plates. It must, then, be borne in mind that the word 'preservative' is only employed for want of a better.

Drying the Plate

Ordinarily speaking, the film is allowed to dry spontaneously, for which purpose a cupboard or box should be fitted up in the manner described in the various handbooks. Another plan that may be adopted by the student, if the plate be not too large, is the use of the hot-air bath, employed in chemical laboratories. The author has found that up to $8\frac{1}{2} \times 6\frac{1}{2}$ inches this method is useful. It is found convenient to allow the doors to be left open till the surface moisture has disappeared, after which they may be closed and the plates be allowed to dry at the higher temperature. Half a dozen plates may be dried by this means in half an hour.

Gum-gallic Process

Of dry-plate processes, only two will be described in detail; descriptions of others can be found in various practical works on the subject. The first that will be described is the gum-gallic process, as introduced by Mr. R. Manners Gordon. His directions are given, and if carefully attended to will give negatives of unequalled harmony.

To any ordinary collodion, 2 per cent. of cadmium bromide is added. The plate having been given a substratum, as shown at p. 160, is coated with this collodion and immersed in the sensitising bath, and allowed to remain in it from seven to ten minutes, according to the temperature. This length of contact with the solution is sufficient to allow most of the bromide to be converted into the silver compound. The washing should be of a thorough nature; the longer the plates have to be kept, the longer it should be continued. The preservative made as under is next applied, by floating it over the surface of the plate.

1.	Gum arabic	7 grammes
	Sugar candy	1·75 grammes
	Water	120 c.c.
2.	Gallic acid	1 gramme
	Water	40 c.c.

These two solutions are mixed in the above proportions.

No. 1 is best prepared by the aid of the heat of a water-bath. The following arrangement (fig. 31) will be found useful in its preparation, as well as in numerous other cases:

C is a water-bath two-thirds filled with water; on the top are rings of varying diameter, fitting into one another, in one of which the flask A, containing the gum-water and sugar-candy, is placed. A small funnel (B) is dropped into the neck of the flask, in the conical part of which a portion of the steam condenses and runs back into the flask. This prevents too great a diminution of the liquid whilst the gum is in the act of dissolving.

The mixed solutions should be filtered, but in this operation great difficulty is often found. The most ready method of effecting it is by the aid of a Bunsen water-pump; by an aspirator of the usual form; or by an exhausting syringe. The arrangement adopted will be seen from fig. 32. The pump, or other exhausting apparatus &c.,

is attached to india-rubber tubing. It is preferable to filter the solution whilst warm; when cold the pores of the filter-paper are rapidly filled up, and the solution refuses to pass. It may be necessary to fix into the funnel a platinum foil cone, made by cutting a piece of

FIG. 31.

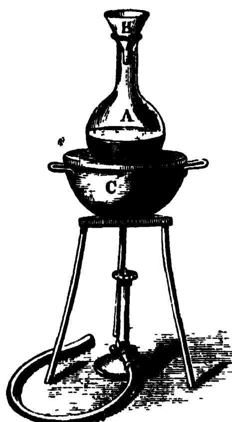
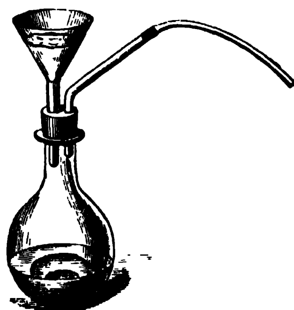


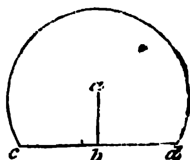
FIG. 32.



platinum foil in a circle, and cutting off a sector, as indicated in fig. 33. In any case the filter-paper should be thin and free from iron.[1]

The preservative solution is floated over the plate, and, after remaining on about a minute, is allowed to dry. If the surface appear dull, it should be dried by artificial heat previous to exposure in the camera.

FIG. 33.



The exposure varies according to the developer employed. In developing a plate by any method, it is usual to apply a narrow edging of india-rubber solution round the

[1] This may be detected by moistening it with hydrochloric acid, and letting fall on it a drop of potassium ferrocyanide.

plate by means of a piece of stick, or by a piece of blotting-paper held in the fingers and run round. A prettier piece of apparatus which is sometimes employed to give the edging is the following: A camel's-hair brush, B (fig. 34), is held in position by a couple of wire loops, C C, inserted in a stick, A, and so arranged that the brush may be lowered into the solution without wetting A. The bottom edge of the stick is brought against the edge of the plate, so that the brush rests on the film, and having drawn round the plate, a neat edging is given. The strength of the india-rubber solution may be five times that given on p. 161. If the first developer be used the exposure may be from four to twenty times that required to give an ordinary wet plate, whilst if the alkaline developer be employed it will develop well with the exposure of a wet plate.

FIG. 34.



Acid Iron Developer.

Ferrous sulphate	2 grammes
Water	30 c.c.
Gelatine	4 grammes
Glacial acetic acid . . .	60 c.c.
Water	400 c.c.

The gelatine may be dissolved in the water, and the glacial acetic acid added to it. This is quite as effective as dissolving the gelatine first in the acetic acid, and the solution is much more quickly made. Three parts, by measure, of No. 1 should be mixed with 1 part, by measure, of No. 2, and after filtering the developer is ready for use. It is better to mix them only a short time before they are required, as a slight precipitation takes place if they be kept long together. To every 4 c.c. of the developer 1 drop of a 60 per cent. solution of silver nitrate should be added, and the application be immediately made to the plate.

The following is the alkaline developer which may be employed :

1.	Ammonium carbonate . . .	5 grammes
	Water	30 c.c.
or,		
	Ammonium hydrate, ·880 . .	1 part
	Water	16 parts
2.	Potassium bromide . . .	1 gramme
	Water	35 c.c.
3.	Pyrogallic acid	1 gramme
	Alcohol	5 c.c.

With this the following proportions :

No. 1 solution		4 parts
,, 2 ,, . . .	2 parts (1 part in cold weather	
,, 3 ,, ...		1 part

These are well mixed immediately before use, and after the plate has been moistened by water are flowed over it. If the exposure has been of right duration the image should immediately appear, in which case the solution should be flowed back into the developing cup, and the detail be allowed to 'come up' by the small quantity remaining in the film. When this is secured another part of No. 3 may be added, and density will gradually be attained. The writer prefers not to give the full density by the alkaline solution, but rather to gain it by the application of the pyrogallic acid intensifier with the silver nitrate solution (see p. 156). If this procedure be adopted, the development should be stopped immediately all the detail is visible by reflected light, and the surface should be flooded with a 1 per cent. solution of acetic acid in water. The intensification next proceeds as in the ordinary bath dry-plate processes.

With an under-exposed picture, if the detail does not appear with the above proportions of the alkaline developing solution, a new mixture is made, nearly all of No. 2 solution being omitted. Unless the exposure be very much under-timed, this is usually efficacious. With an over-exposed picture the image will flash out ; the developer must

at once be washed off, and a double amount of No. 2 added, or resort may at once be made to the acid intensification.

The following is the preparation known as the ferrous oxalate developer :

1.	Ferrous sulphate	10 grammes
	Water	30 c.c.
2.	Potassium oxalate . . .	10 grammes
	Water	30 c.c.

One part of 1 is mixed with 3 parts of 2 in order to form the ferrous oxalate mixture.

The ferrous sulphate is decomposed by a portion of the potassium oxalate, and the remainder holds the ferrous oxalate thus formed in solution. To make up a developer suitable for developing the dry plates in question the following should be used :

Ferrous oxalate solution . .	4 parts
Potassium bromide solution in water, 10 per cent. . . .	½ part

These are well mixed, and, after washing the plate, are to be applied. As a rule good density will be attained with it, but the image may require intensification as before. The ferrous oxalate solution may be made by dissolving dry ferrous oxalate in a saturated solution of potassium oxalate in water, but as the solution thus made rapidly deteriorates it is recommended that the above preparation should be employed, since it is then always used in a fresh condition.

In order to develop the image the plate should be immersed in water of not less than 16°C. If the iron developer be employed the time of immersion should be two or three minutes, whilst if it be the alkaline developer a mere moistening is sufficient. The method to be adopted with the former is that already described. When the detail comes well out, the intensification of the image is given by the ordinary pyrogallic acid solution (p. 151). These plates are excellent when employed in a fairly dry climate, but they are disappointing when much atmospheric moisture is

present; the gum softens and absorbs water, giving rise to spotty pictures. This seems to be due to a fungoid growth upon the gum, and there is no apparent remedy for it.

The negatives taken by the gum-gallic process, under favourable circumstances, are everything that can be wished for, being delicate, full of detail, having the well-known bloom, and being fairly sensitive even with the iron developer. In the hands of Manners Gordon it has proved the most trustworthy of any bath dry-plate process (except one) with which that eminent photographer has worked.

Albumen Beer Process

This process has been fully described in another work by the writer,[1] and is given as therein described. It was introduced by him for solar photography, and was employed by the English Transit of Venus expedition. It is, however, equally adapted for landscape work, and is very certain in its results. The collodion employed can be that described at p. 138, though for more rapid work the following is better:

Alcohol, ·825	450 to 350 c.c.
Ether	350 to 450 c.c.
Pyroxyline	12 grammes
Ammonium iodide . . .	3·5 grammes
Cadmium bromide . . .	9·0 grammes

The relative proportions of ether and alcohol are adjusted according to the temperature in which the plates have to be prepared.

With the ordinary samples of collodion the usual silver nitrate bath (p. 146) can be used, but with the collodion made as above it is advisable to use a bath containing 16 per cent. of silver nitrate. In both cases rapidity is increased by the addition of 2 per cent. of uranium nitrate. It has been found advantageous to dip the plates at first in the weaker bath, allowing them to remain in it for a couple

[1] *Instruction in Photography.* Sampson Low, Marston & Co.

of minutes, and then to transfer them to the stronger for ten minutes more. This mode of procedure gives very sensitive and opaque films, the greater part of the actinic rays being thus utilised. The sensitiveness, however, greatly depends upon the porosity of the film, and every effort should be made to attain the maximum of this quality without injuring the texture of the film. The addition of the largest practicable amount of water to the collodion tends to give this desired porosity. After sensitising, the plate is slightly washed, and the first preservative applied, which is—

Albumen	100 c.c.[1]
Water	100 c.c.
Ammonium hydrate . . .	12 c.c.

This is beaten up into froth (or is mixed by pounding it in a mortar with silica), and, when settled, the clear liquid is decanted off. The solution is mixed, immediately[2] before use, with an equal quantity of ordinary beer or stout, and floated over the plate. When bottled beer is used, it is advisable to drive off all the carbonic acid by a gentle heat. The excess is drained off, and the film thoroughly washed under the tap for a couple of minutes, and is finally rinsed with a solution of plain beer, to which 1 per cent. of pyrogallic acid has been added.

The plate is dried in the ordinary manner.

The exposure with well-prepared dense plates is often as short as that necessary for wet plates, but great latitude is admissible. With 20 times the minimum exposure necessary to secure a good negative there need be no danger of veil.

The development need not be effected for at least a

[1] Dried albumen—5 grammes to 100 c.c. of water—may be substituted for the 100 c.c. of albumen.

[2] This precaution is necessary, otherwise the tannin of the beer is precipitated by the albumen.

month after exposure. The following solutions are those employed :

1.	Pyrogallic acid . . .	1 gramme
	Water	40 c.c.
2.	Ammonium hydrate, ·880 .	1 part
	Water	4 parts
3.	Citric acid	4 grammes
	Acetic acid (glacial) . .	2 c.c.
	Water	30 c.c.
4.	Silver nitrate . . .	1 gramme
	Water	20 c.c.

The description of the development is taken from the work already referred to.

'The washing water before development should be of a temperature not less than 15°C. When the plate is washed, the following developer is employed : To each 50 c.c. of No. 1 are added 10 drops of No. 2, and after well mixing with a stirring rod the solution is floated over the plate.

'Almost immediately the image begins to appear, and after a few seconds' interval the detail can be seen by reflected light to gradually develop. Another 7 drops of No. 2 are again added to the solution, which is once more floated over the plate. Twenty drops of No. 3 are next poured into the developing cup, and the solution from the plate poured into it. Again the plate is rinsed, this time by the acidified pyrogallic solution, and intensification given by the use of it with a few drops of No. 4. It is not advisable to allow too much detail to come out with the alkaline solution, but to allow a portion of it to be brought out by the subsequent treatment with pyrogallic acid and silver. The alkaline developer reduces the bromide salt, and leaves the iodide to be attacked by the silver solution. It will be remarked that no restrainer such as bromide is employed ; the albumen dissolved by the ammonium hydrate plays the part of a retarder, but not as a destroyer of the latent image.

When the image appears sufficiently dense, it is fixed by either sodium hyposulphite or by potassium cyanide.'

One point in the preparation of these plates cannot be too strictly attended to, viz. to keep the fingers away from all contact with the film during preparation. A touch, however slight, will cause a stain, and unsightly markings extending across the plate have been traced to the same cause.

CHAPTER XVIII

COLLODION-EMULSION PROCESSES

We now come to a class of collodion dry-plate processes which differs from those which have been described, inasmuch as in it the sensitive salt of silver is held in suspension in the collodion. When such an emulsified collodion is poured upon the plate, we obtain a film capable of receiving an invisible impression. The emulsion is principally formed with silver bromide, though certain other additions are sometimes necessary in order to ensure clearness in working. The silver bromide is introduced into the collodion by dissolving some soluble bromide in it, and then gradually adding an alcoholic solution of silver nitrate, the amount of which may be either in defect or excess of that necessary for the complete conversion of the whole of the soluble bromide. It is found practically that silver bromide is most sensitive when exposed in presence of an excess of silver nitrate, but most prone to give veiled images, whereas if the soluble bromide be in excess a developable image is formed less rapidly, but greater freedom from fog is secured. Some of the probable reasons for this may be gathered from chap. vi. In preparing an emulsion, it is rarely possible to hit the exact proportions which shall give neither excess nor defect in one or other of the emulsion-forming constituents, and so to secure great sensitiveness with clearness; hence it is

always better so to arrange the proportions that one or other shall be in known excess.

The following experiments may be made with advantage, in order to see what will be the result of having excess of the soluble bromide or of silver nitrate.

Prepare bromised collodion as given for the first process (described p. 176), and to 100 c.c. add, in the first case, 6 grammes of silver nitrate; and to another 100 c.c. the quantities given. After leaving for twenty-four hours, coat plates with these two specimens respectively, exposing before the collodion has become dried. Note their behaviour with the alkaline developer (see p. 168). It will be found that with the plate in which there is excess of bromide there will be no developable image, whilst with that prepared with excess of silver nitrate there will be a fog over the image. Next take plates prepared with the same collodions and wash thoroughly under the tap. Both now will give good developable pictures, but that having an excess of bromide will require a longer exposure to give a good negative. Next, take similarly prepared plates, and, after washing, flow over them a solution of tannin, and the images will be found to be more readily developable. Again, prepare an emulsion as before, using a soluble metallic chloride instead of the hydrochloric acid, and, having divided it into two portions, add an excess and defect of silver to them respectively. Prepare plates as above, and notice the behaviour. It will be found that with the slightest excess of silver there will be inevitable fog, whilst with the defect the behaviour will be the same as that given above. Perhaps the most sensitive emulsion may be prepared by having a slight excess of silver nitrate and nitric acid, omitting the chloride altogether.

The use of silver chloride in the emulsion secures density; it does not of necessity secure freedom from fog, but, being more soluble in ammonia than the bromide, the ammonium pyrogallate readily dissolves it, and immediately precipitates it on the parts acted upon by light. It is

believed that this simple explanation is capable of rendering clear the use of it, as recommended by various writers. The following rules may be laid down :

1st. That nothing but silver bromide is necessary to give a good image, if the soluble bromide be in excess.

2nd. That if there be an excess of silver nitrate, the emulsion must be acidified with nitric or other mineral acid, or be neutralised by certain metallic chlorides, to secure freedom from fog.

With regard to the first part of this second rule, it will be remarked that the same necessity arises in the bath processes where much bromide is present in the collodion. It must also be borne in mind that if the first rule be followed, the density of the developed image will be strong ; whilst if the latter (unless chloride be present), it may be weak, unless some density-giving body, such as silver nitrite, glucose, &c., be added to the emulsion, in which case good density can be obtained.

Having made an emulsion as described, it will be well to make another simple experiment. Coat a plate with it, and allow it to dry. On drying, it will be found that the soluble salts have crystallised on the surface of the plate, rendering the development of an image almost impossible. Here we have evidence that it is necessary to remove these salts. There are two ways of accomplishing this, either by washing the plate after being coated with the collodion, or by washing the whole bulk of the emulsion after allowing it to gelatinise by evaporation of the solvents. In the last method the washed emulsified collodion is dried, and the resulting pellicle is again dissolved in ether and alcohol. It has certain advantages about it which cannot be gainsaid ; thus, the sole manipulation in getting ready a dozen dry plates is to coat them with the emulsion, and then allow them to dry. It also has drawbacks ; one of the principal of which is the liability to spots on the negative, a point which is difficult to understand, since they

probably will be entirely absent on plates prepared with the same emulsion unwashed.

It is not proposed to enter into details of all the different varieties of the emulsion processes : two distinct variations will be given, one of which will be typical of an emulsion where the coated plate alone is washed, and the other of a washed emulsion. Both these will be of the simplest character, and have succeeded in the hands of the writer.

UNWASHED EMULSIONS

Canon Beechey's Process

The following are Canon Beechey's directions, which if followed will give tolerably certain results. Take

Cadmium bromide (dried) . . .	90 grammes
Alcohol, ·805	1 litre

and allow the mixture to stand, and then decant from it any quantity that may be required. To each 100 c.c. of it add 1·6 c.c. of strong hydrochloric acid.

Of the above solution take . .	50 c.c.
Ether, ·720	110 c.c.
Pyroxyline	2 to 2·5 grammes

The pyroxyline should be that prepared at high temperature, and may contain nitro-glucose if thought advisable (see p. 132). It will be found necessary that it should stand at least a day before being used ; filtering through tow only partially frees it from small particles of undissolved cotton. If much of the emulsion is likely to be required, one of the tall graduated glasses, as in fig. 35, will be found convenient ; any quantity can then be syphoned or decanted off.

When the collodion is clear it is ready for sensitising : that part which is to be emulsified should be poured into a glass beaker. For every 100 c.c. of the above, take 5·6

grammes of silver nitrate and powder it carefully in an agate mortar, or by means of a glass stopper on a thick sheet of glass. Place it in a test-tube, with *just* sufficient water to dissolve it, and add to it 30 c.c. of alcohol, ·805. This alcoholic solution of silver nitrate should be added to the collodion (fig. 36) drop by drop, and the emulsion should be stirred continually whilst the additions are made; finally, the test-tube should be rinsed out with another 30 c.c. of alcohol, and added to the collodion.

FIG. 35.

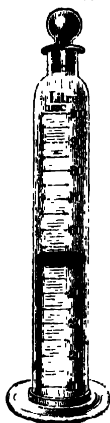
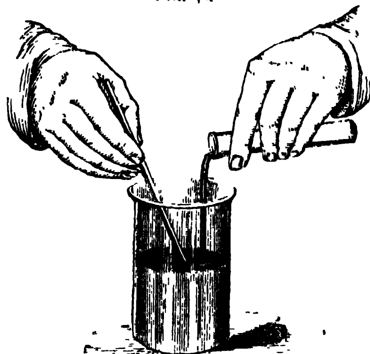


FIG. 36.



After the final addition the emulsion should be very smooth and rather thick, though when poured upon a strip of glass it will appear of a transparent nature. After keeping twenty-four hours, however, it will be creamy, and appear of an orange colour when a candle flame is viewed through small layers of the liquid. This colour is indicative of a proper preparation of the emulsion, showing that the silver bromide is in a very minute state of division.

It is possible to cause an emulsion to have a decidedly bluish-green tint, in which case the particles seem to be in a

different state of aggregation from that when the ruddy tinge is seen. When further improvements in the emulsion are made, it may be that this blue tint will be the mark of a more sensitive preparation. This emulsion should be used soon after the creamy state is attained, as otherwise it will again become thin, and the silver bromide will rapidly precipitate on the bottom of the bottle.

The plate having been coated with a substratum or edging (see p. 160), the collodion is applied in exactly the same way as is the unemulsified collodion for the wet process. It is necessary that the emulsion should be rendered homogeneous, otherwise the film will appear granular. This is effected by shaking it in the bottle half an hour before it is applied to the plate. When the collodion is set, it is immersed in a dish of distilled water or filtered rain water till all the repellent action between the solvents and the water is eliminated, and till the great excess of silver nitrate and the other soluble salts is washed out. It may then be passed through another dish of water if found necessary, and finally allowed to rest in a dish containing beer, to every litre of which 2 grammes of pyrogallic acid has been added. The best kind of beer is that known as sweet ale, the saccharine and gummy matter being more abundant in it than in that known as bitter ale. Any trace of silver which may remain in the film combines with the organic matter, and the danger of veil is thus reduced. The drying is conducted in the usual manner, care being taken not to disturb the plates till they are thoroughly desiccated.

If the calculation as to the amount of silver nitrate necessary to combine with bromide and hydrochloric acid be made, it will be found that there is a considerable excess of silver nitrate in the above emulsion. The organic matter of the preservative is present to give intensity during development.

The development will be carried out by the alkaline

method given at p. 168, or the ferrous oxalate at p. 169, the whole of the descriptions applying to the process under consideration.

CHAPTER XIX

WASHED COLLODION EMULSIONS

We now come to the class of washed emulsions. There are almost endless varieties of preparation, but experience seems to show that the simpler the formulæ are kept the more certain are the results. The following is a mode of preparation which has almost invariably given rapid and excellent results, and the writer strongly recommends it.

The plain collodion is prepared as follows :

Ether, ·730	50 c.c.
Alcohol, ·820 to ·830	25 c.c.
Zinc bromide	5 grammes
Pyroxyline	2·5 to 3·5 grammes

The variation in the amount of pyroxyline is given, as on its quality largely depends the amount which is essential. With ordinary pyroxyline the smaller amount will suffice, whereas, if it be of a short pulverulent class, the larger quantity will be necessary. The writer recommends the ordinary tough pyroxyline, prepared from ordinary cotton previously boiled in strong alkali, and in the strength of acids given at p. 130. The zinc bromide may be dissolved in the alcohol, with a small amount of water in addition, if found necessary. To the above quantity of zinc bromide should be added about 30 drops of nitric acid, or 1 small drop of bromine. The reason for either of these additions has already been given. If the bromine be employed, care should be taken to estimate the quantity of silver nitrate with which it will combine. This may be conveniently

executed by dropping, say, 3 drops into 50 c.c. of water, and precipitating with a standard solution of silver nitrate, or by taking care to have an excess of silver, filtering, washing the precipitate, and gently igniting it, in order to convert the silver bromate into silver bromide, and then weighing it.

When the bromised collodion is perfectly clear from all floating particles, which can be secured by allowing them to settle, or by filtering them through cotton which has been previously well washed and rinsed with alcohol, it is ready for the addition of the silver nitrate. It is well to allow an excess *at least* of ½ per cent. of the silver salt if great sensitiveness is required, otherwise the bromide may be allowed to be slightly in excess. To convert the above amount of zinc bromide into silver bromide would theoretically require 7·56 grammes, but in practice it is found that this amount cannot be depended upon. When nitric acid is used with the zinc bromide it will be found that 8·5 grammes suffice. When the bromine is used the amount required must be subject to experiment. The student may find it convenient to add the silver nitrate solution little by little till he hits the point where an excess commences, and then to add ½ per cent. more of silver nitrate. To ascertain when the excess occurs, a drop of the emulsion, from time to time between the additions of the silver nitrate solution, should be poured on to a glass plate, and a little potassium chromate dropped on to it; the slightest excess is shown by a red coloration due to silver chromate.

The silver nitrate is dissolved up as in the last process, and poured in as already described. It may be as well to note that finer-grained emulsion is sometimes made by keeping out half the collodion, adding the whole of the silver little by little, and then stirring in the other half of the collodion.

In order to obtain a maximum sensitiveness, the emulsion should be left for from twenty-four to sixty hours, the time depending much on the kind of pyroxyline employed. If a

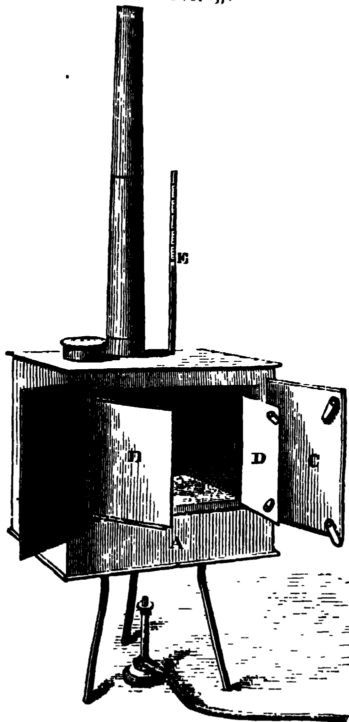
large batch of emulsion is to be made up, it may be advisable to prepare 50 c.c. first, and at the expiration of twenty-four hours, forty-eight hours, sixty hours, to wash it as directed below, and test its qualities; and a note should be made of the period at which it seems most sensitive, and at the same time free from fog. It is noteworthy that the washed emulsion usually appears to possess the same qualities as the unwashed. If, therefore, this process of testing be considered too tedious, the emulsion may be tested at intervals in the unwashed state, or, to speak more correctly, after it has been washed after coating the plate. When the emulsion is in a proper state, it should be poured out into a flat dish, and be allowed to set. A gentle agitation with a glass rod causes more surface to be exposed, and the evaporation consequently takes place more rapidly. In a moderately warm room half an hour will generally suffice to render it in a condition fit for the subsequent washing. This may be known by the glass rod separating the gelatinous mass in flaky pieces, which retain their shape after a minute's interval.

The emulsion is next covered with distilled or pure water, and allowed to soak for two or three minutes, when the liquid is drained off, and the emulsion transferred into a jar, and again covered with water. After stirring well, and allowing a time to elapse (say fifteen minutes) in order that the water may penetrate into the interior of the mass, it is again drained off and replaced by fresh water. This washing is continued till the wash water, treated with hydrochloric acid if an excess of silver have been employed, or with silver nitrate solution if excess of bromide have been employed, shows only a *slight* opalescence. It is important that the washing be done rapidly, as long soaking of the gelatinous emulsion is greatly detrimental to securing density of the image when alkaline development is employed. The reason of this lack of density seems to be that some small portion of the precipitated pyroxyline is soluble in

water, and that it is this organic substance which causes the silver to be reduced in the film to such a state of subdivision as to cause opacity.

When the washing is complete, the emulsion pellicle is pressed between blotting-paper in order to get rid of the greatest part of the water which is occluded in it, and is allowed to dry spontaneously or by the aid of heat.

FIG. 37.



The first mode of drying is the safer, as it sometimes occurs that the heat of even a water oven (fig. 37) is sufficient to shrivel up the pellicle to such an extent that it becomes very insoluble in a mixture of ether and alcohol. The procedure that the writer recommends is to allow it to become *nearly* dry in the water oven, and then to allow the last remains of water to evaporate spontaneously. A slight quantity of water is not hurtful to the emulsion, and if, after hard pressure with a spatula on a square of the pellicle, there is not sufficient moisture to damp blotting-paper, it may at once be transferred to a bottle to redissolve. The bottle employed should be capable of holding twice the amount of solvents that will be used, as space is required for shaking.

The solvents employed are equal parts of pure ether and absolute alcohol, 100 c.c. being employed for every 1¾ gramme of pyroxyline employed.

With some pyroxyline the resulting images are deficient in vigour. To correct this, to the first wash water a strong solution of tannin, or salicine, &c., may be added.

A modification of the above emulsion may be prepared by emulsifying with an excess (say 5 grammes) of silver nitrate, after 15 to 20 drops of strong nitric acid added to each 100 c.c. of the collodion. After the addition of the excess of silver nitrate a sufficient quantity of some metallic chloride, such as of cobalt, may be added, in order completely to neutralise that excess of silver, and to leave a slight excess of the soluble chloride. This method is due to Mr. Newton, and in his hands appears to work satisfactorily. The presence of a free chloride is not so destructive of sensitiveness as the free bromide, hence the preference that is given to the former over the latter for neutralising any excess of silver nitrate. It is often useful to keep the pores of the collodion open by a little resinous matter, such as gum ammoniacum. This gum is very insoluble, and, if employed, a saturated solution of it in alcohol should be prepared, and the resulting varnish should replace the alcohol employed for redissolving the emulsion pellicle. With all the washed emulsion processes the plate is coated as with ordinary collodion and allowed to dry, no preservative being necessary. The dark heat which is radiated from a slab of iron placed over a spirit lamp or Bunsen burner is recommended by Mr. Woodbury, to cause the rapid evaporation of the solvents from the coated plate. The plate must not be exposed to the naked flame from these sources, as the blue colour is sufficiently intense to cause a veil to spread over its surface on development. Washed emulsion plates will keep indefinitely both before and after exposure, as will the emulsion if all excess of silver nitrate be washed away. The exposure necessary is largely dependent on the presence of

soluble bromide or chloride and on their quantity. As a rule the plates require half as much exposure again as a wet plate.

The development is conducted as laid down for the previous process, and calls for no especial remark.

CHAPTER XX

PAPER NEGATIVES

HAD the historical order of photographic processes been followed, the calotype process would have been described immediately after the daguerreotype process, but it seemed more likely that the details of the former would be better understood after a study of the collodion wet and dry processes. The original process which Fox Talbot introduced has been but little improved, and it is therefore given nearly as he described it, modifications being suggested where necessary.

The paper employed should be as tough and grainless as possible, capable, however, of holding sufficient of the sensitive compound to give a body to the image. Good English paper of the consistency of medium saxe answers every purpose. The great drawback to all papers of the present day seems to be the chance of transparent spots appearing during development, and a consequent damage to the image. What is the chemical nature of these spots is not known, but they can generally be got rid of by brushing a dilute solution of hydrochloric acid over the surface of the paper, and then thoroughly washing off all excess of acid. When dry the paper is ready for impregnating with silver iodide. This last is formed by taking:

No. 1.	Silver nitrate	3 grammes
	Distilled water	20 c.c.
,, 2.	Potassium iodide . . .	3 grammes
	Distilled water	20 c.c.

No. 2 is poured into the solution of No. 1 with constant stirring, and a precipitate of silver iodide is formed. The potassium iodide being in slight excess, a certain quantity of the silver iodide is held in solution. The precipitate is allowed to settle at the bottom of the glass measure (in which we will suppose the two solutions to have been mixed), and the supernatant liquid is poured off; water is again added, and after stirring it is again poured off. This operation of washing is continued some three or four times, or until the soluble potassium nitrate is nearly eliminated.

The silver iodide is next dissolved in a solution of potassium iodide:

Potassium iodide . . .	30 grammes
Water	60 c.c.

This is poured on the silver iodide and well stirred. As this quantity will not effect complete solution, crystals of the potassium salt must be added till after much stirring the solution is semi-transparent or milky.

The paper is next cut to a convenient size, and is pinned on a flat board. The solution is applied by a brush of cotton wool, a good form adapted for the purpose being given in the figure. A is a glass tube of about 20 centimetres long, and above 1 centimetre diameter. A loop of string, B, passes through the tube, across which is placed a thin tuft of cotton wool, C. The loop is then pulled up into the tube, a sufficiency of cotton wool being allowed to remain externally to form the brush. It is advisable first to wash the wool in a weak solution of alkali in water, taking care, however, that none of the alkali remains in the fibre, and that it is thoroughly dried before being used as a brush.

FIG. 38.



The solution is brushed up and down and across the paper, till the whole surface has received a uniform coating of the dissolved iodide. When partially dry the paper is immersed in a dish of distilled water, all air-bubbles being

carefully removed from the surface. After soaking for a couple of minutes it is removed to a second dish, and subsequently to a third dish. The water removes the potassium iodide, and leaves a primrose-coloured silver iodide on the surface of the paper. After the washing has been continued two or three hours, the paper is hung up and dried. In this state it is nearly insensitive to light (though not quite so, as the iodide is in the presence of organic matter), and can be stored away between the clean *unprinted* leaves of a book. When required for use, the paper is pinned on to the board as before, and a mixture of the following solutions is brushed over it:

No. 1.	Silver nitrate	5 grammes
	Glacial acetic acid . . .	8 c.c.
	Water	50 c.c.
,, 2.	Saturated solution of gallic acid in distilled water.	

To every c.c. of No. 1 add 60 c.c. of distilled water, next 1 c.c. of No. 2, and finally 30 c.c. of distilled water. If the temperature be high the water must be increased to such an extent that immediate reduction of the silver nitrate may not take place. After well mixing, the solution is applied lightly, but plentifully, to the iodised paper with the cotton-wool brush already described, and all excess blotted off on filtering-paper of the purest description. Two sheets are then placed back to back with blotting-paper between them.

The paper is most sensitive in its moist state, but it is also capable of giving pictures when dry, or until the surface of the paper becomes discoloured by a reduction of the gallate of silver. For exposure in the camera a sheet may be placed between two pieces of glass, or the corners may be gummed on to a sheet of glass, the paper taking the position of the collodion film of the ordinary processes. The exposure varies considerably, according to the preparation of the paper; and it should always be sufficiently prolonged to give a trace of the sky-line on the undeveloped paper. To develop the picture, the paper must be pinned on the board as before, and equal parts of No. 1

and No. 2 applied, with similar quantities of water as already indicated. This is applied with the brush, and is continued till the developing action begins to flag. When this is the case, the gallic acid solution, No. 2, is applied very lightly, until the deep shadows begin to dim by transmitted light. The development must now immediately be arrested, otherwise the picture will be veiled.

For an under-exposed picture more of No. 1 should be used than that given, and if over-exposure be feared (indicated by the picture being fairly visible), No. 2 should be in excess. A little consideration of these points will show how development may be equalised in dark parts. An artist in the production of these pictures will be able to produce *a picture* by a little attention to the above details, whilst a mere manipulator would probably produce nothing but an image wanting in delicacy and gradation.

The negative is fixed by immersion in a sodium hyposulphite solution :

Sodium hyposulphite . . .	60 grammes
Water	1 litre

The fixing being complete, which may be known by a total disappearance of the yellow of the iodide when the paper is viewed by transmitted light, the picture is washed in abundant changes of water until all the hyposulphite is thoroughly eliminated. This may be known by applying the test given at p. 206. The washing should take at least three or four hours even in running water.

It may be advisable to call attention to the necessity of the addition of acetic acid to the sensitising solution. This is always advisable in warm climates, as it greatly restrains the reduction of the silver nitrate; the less added, however, the more sensitive the paper will be.

When the paper negative is dry it is ready for waxing. A flat-iron (preferably a box-iron) is heated to such a temperature that it will readily melt white wax. A cake of this substance is brought in contact with the iron whilst the

latter traverses the paper. The whole of the picture, except the sky, should be rendered translucent by it. The superfluous wax is absorbed by blotting-paper placed upon the negative, over which the hot iron is passed. It is a mistake in this last operation to heat the iron too much; overheating causes the blotting-paper to take up too much of the wax, and leaves the grain of the paper visible. It sometimes happens that yellow spots occur in the whites of the picture. These are generally removable by the application of a dilute solution of hydrochloric acid. It need scarcely be remarked that this entails a thorough washing. The acid must never be applied till all the sodium hyposulphite is thoroughly eliminated, for if any remain in the paper it is decomposed by the acid, and the inevitable result will be a fading of the picture. Further remarks on this subject will be found in the chapter on silver printing.

There are various processes for the production of paper negatives extant, amongst which may be mentioned those of Le Gray, Blanquart-Evrard, and Prichard. That due to Le Gray was at one time a great favourite, its distinguishing feature being that the paper is waxed before being sensitised. The waxed paper is immersed in a solution of potassium iodide and bromide, together with sugar of milk, and after drying is treated with a solution of silver nitrate, acidified with glacial acetic acid. The development is carried on much in the same way as that indicated in the above process, the paper being submerged in the fluid. This last process, perhaps, is better adapted to careless manipulation than that described above, as all danger of staining the back of the picture is avoided.

There are several negative and positive papers in the market at the present time, some of which are very excellent. The method of holding these papers *in situ* in the camera will be given in the chapter devoted to apparatus. After using the ferrous oxalate developer before washing, we usually pass the paper through a bath of water which has been

rendered slightly acid by hydrochloric or sulphuric acids. This prevents the formation of any oxide of iron in the water, and removes the oxalates. The negative after well washing is fixed and again washed. The paper is rendered translucent by waxing, or by applying crude paraffin to the back.

CHAPTER XXI

SILVER PRINTING

In the fourth chapter the results of the action of light on silver chloride and organic compounds of silver were shown. In this part it is proposed to treat the subject rather more fully, as silver printing entirely depends upon it.

The student would do well to make the following experiments for himself, as by so doing the rationale of the variations in the processes will become familiar to him, and many failures will be avoided by a study of the theory.

Take any ordinary paper which contains size of some description, and immerse it in a solution of sodium chloride :

Sodium chloride	1 gramme
Water	50 c.c.

Hang it up and allow it to dry, and in non-actinic light (adopting the manipulations which will be presently described) float several pieces of convenient dimensions on a solution of silver nitrate for three minutes :

Silver nitrate	5 grammes
Water	50 c.c.

When dry to the touch, place one of these pieces under a negative in a printing frame, and expose it to the action of the sunlight ; after a few seconds open the frame in a subdued light, and note the result. The parts acted upon by light will have a violet tint, and if ammonia

be applied to a portion of the darkened paper it will be found that the image almost entirely disappears. For reasons already given this will indicate that the silver chloride is dissolved. Allow further play of sunlight, say for a couple of minutes, and again note the result. It will be found that the image is much redder in colour, and that ammonia fails to remove all the coloration. From this we infer that the organic compound formed by the size of the paper and the silver nitrate is acted upon by light. Next take another sheet of the same paper and wash out all excess of silver nitrate, and expose under a negative, and examine the print at the same intervals as before. It will be found that the short exposure produces hardly any perceptible darkening, whilst with the longer it is much less than in the previous experiment. From the results of experiments already detailed in the fourth chapter, it will be seen that the absence of silver nitrate prevents the darkening of the silver chloride, and that the organic compound is the more impressionable. A minute examination of the image will also show that there is a spotted irregular appearance in the darkest parts. There is an easy theoretical explanation of this. The chlorine liberated from the darkening silver chloride is taken up by the organic compound, bleaching it to a certain extent, forming white chloride of silver, which in its turn is capable of being acted upon by light. Experiments with similarly washed paper will show that, though the first darkening is much slower than in the unwashed paper, yet the action on the former approaches more nearly the rapidity of the latter, as the organic silver oxide, which is greedy of chlorine, is formed. Next, fix these paper images by immersion in the bath of sodium hyposulphite, as given at a subsequent portion of this chapter. Both prints will assume a foxy-red colour, that containing no free silver nitrate losing least in depth. The reason will be apparent. The silver sub-chloride, Ag_2Cl, formed is soluble as far as one atom of

silver and one atom of chlorine are concerned (AgCl), leaving behind one atom of metallic silver. Since it is only the surface of a particle of silver chloride that is blackened, the darkening of the compound is in itself a protection from the penetration of light into it. It can be shown that the depth to which such penetration can take place with ordinary exposure is very superficial, hence the metallic silver left behind must be exceedingly minute; so small is it indeed that the most delicate balances are too coarse to weigh it. It may be of interest to note an experiment which was carried out to test this. One thousand square centimetres of a glass plate were coated with a layer of silver chloride held *in situ* by inert collodion, and exposed to sunlight in the presence of an excess of silver for five minutes. The original amount of chloride was 102 centigrammes, and after fixing in the bath the metallic deposit was dissolved off in nitric acid, and estimated volumetrically, and found to give only 55 milligrammes of metallic silver.

The organic substances employed in printing may now briefly be considered. Albumen undoubtedly comes first, owing to the properties it possesses of giving a good tone when converted into albuminate of silver if in contact with silver chloride and excess of silver nitrate, and also on account of its insolubility after coagulation.

The formula for albumen is taken as $C_{72}H_{108}N_{18}SO_{22}$, though it can scarcely be said to be established with any certainty. Albumen coagulates in the presence of nitric acid, and also at 65°C. It is precipitated, but not coagulated by alcohol. It combines with the metals, prominent amongst which is the compound it forms with silver. Silver albuminate is white, turning a dark-red brick colour in the presence of white or other actinic lights. The change is speedily effected, and, like other organic compounds of silver, is not dissolved by ammonia after darkening, though the addition of an alkali speedily dissolves the white albumi-

nate. This alone prevents the adoption of an alkaline solution of silver, such as the ammonio-nitrate of silver, for sensitising paper coated with this and some soluble chloride, as the effect would be simply to dissolve it. Gelatine, which is the size used in some papers, combines with silver, and forms a red tint on exposure to light ; it is now largely used in the form of gelatino-chloride paper for printing purposes. Starch ($C_9H_{10}O_5$) forms a compound with silver, which on exposure to light darkens to a more violet colour than either of the preceding. It is largely used in sizing paper, and it is consequently necessary to note this colour.

From the foregoing remarks it will be seen that all the bodies which are employed in sizing ordinary paper will combine with silver. In all printing operations one point is a desideratum, viz. that the image should be on the surface of the paper, and not sunk into it. The importance of this may be tested by sensitising albumenised paper on the reverse side, and endeavouring to obtain a print on the albumen surface in the ordinary manner. It will be found that the image will appear feeble by reflected light, though by transmitted light it will appear well defined and dense. When albumen is used fresh, and in a slightly alkaline condition, the resulting print possesses greater stability than any of the foregoing substances ; as regards delicacy of image it cannot be surpassed. Unfortunately albumen is most easily applied to the surface of paper when slightly acid, the acidity being due to decomposition, and the resulting compounds formed are more liable to change.

It may be asked, why not print in pure silver chloride alone, held *in situ* by some vehicle, such as collodion ? This is not impossible though impracticable, as the reduction of the silver chloride image by the fixing solutions is so great that the print would be wanting in vigour. With the addition of some organic compound, however, it becomes quite feasible ; but then, be it remembered, the depth obtained is due to that

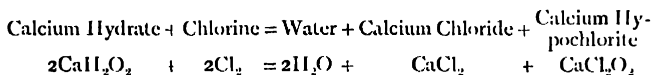
organic substance. Thanks to the discovery of Mr. Wharton Simpson, that silver chloride and some organic compounds of silver (amongst which we may name citrate of silver) will emulsify in collodion, prints are readily obtained by the collodio-chloride, and possess a beauty which cannot be surpassed. In the next chapter this process will be described; merely mentioning *en passant* that in this process, as in any other in which printing on silver chloride takes place, an excess of silver nitrate is beneficial.

The colour of prints obtained is always objectionable if fixed directly after taking out of the printing frame: and resort is had to an operation called toning to render it more pleasing. This toning may consist of gilding the silver image, platinising it, or substituting some other metal for it. The colour of the silver print when appearing through this other metal may give a pleasing tint, or it may fail to do so, according to the extent to which the operation is carried. It will be seen, in the practical instructions in printing, that the picture is more or less washed in water before toning. By immersion in water the violet-coloured image becomes of a red colour: to what this change is due is rather uncertain. It has been held that it is due to the water dissolving a certain part of the silver oxide. It may be due to a different compound being formed by the combination of water with the altered compound, but this is doubtful. In order to tone the picture, certain solutions of gold, platinum, or other metals are made, and the print immersed in them; the first of these metals, in the shape of gold trichloride, is that usually employed. It is therefore proposed chiefly to confine the remarks on toning to that process in which that metal is principally employed. The gold trichloride has the formula $AuCl_3$, which is a fairly stable compound. If its temperature be raised to 170°C. it becomes decomposed, a pale yellow and insoluble powder, gold chloride ($AuCl$), resulting, chlorine being evolved. When the former salt of gold is mixed with a solution of silver nitrate, the chlorine leaves

the gold to form silver chloride, and the latter salt of gold is formed. Acetates, as also the carbonates of the alkalis, are capable of precipitating gold from a neutral solution in the presence of any disturbing cause—such as organic matter.

It will be seen from the formulæ given for toning solutions, p. 203, that one contains chloride of lime, and as an example of one kind of toning this one will be considered. If a print so thoroughly washed that all excess of silver nitrate is eliminated be immersed in this solution, it will be found that the gold deposits very slowly, and that the image becomes feeble and spotted in appearance, whereas with a print in which the excess of silver nitrate has been but partially removed, the toning or gilding action takes place much more readily.

Chloride of lime is a mixture of calcium chloride ($CaCl_2$) with calcium hypochlorite ($CaCl_2O_2$), being made by passing chlorine over calcium hydrate, or common slaked lime.



Now gold trichloride, when uncombined with an alkali, is generally in an acid condition, due to the presence of hydrochloric acid, and in order to neutralise this, calcium carbonate forms part of the toning bath. On immersing the silver print the equilibrium is disturbed, and the gold begins to deposit, and, consequently, chlorine is liberated. In the directions for use of the toning bath it is stated that the solution should be made with hot water if required for immediate use, whilst if made with cold it must stand twenty-four hours. This causes a certain quantity of the hypochlorous acid to be evolved, and leaves a small portion of calcium hydrate in solution.

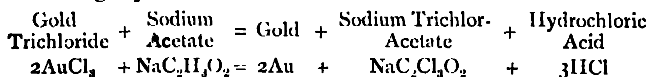
In the case of the thoroughly washed print, the chlorine attacks the silver subchloride or the organic silver oxide, and forms the white silver chloride; for, be it remarked, the

gold which is situated nearest the printed surface is first reduced, and the image is therefore in close proximity to the chlorine, and readily attackable by it. At the same time the silver oxide and subchloride are in proximity to the chloride of lime, which reduces them also to the state of chloride, particularly if it be rich in hypochlorous acid. In the case of the slightly washed print the same action takes place, but we have a new element to deal with. In this case the solution or excess of the silver nitrate held in the pores of the paper gradually becomes diffused to the surface, combines at once with the liberated chlorine, and forms chloride of silver, *but not at the expense of the image.* It will be noticed in toning operations that this chloride is absolutely formed on the surface of the print, and can be removed by a slight rub with the finger. On fixing the print, the silver chloride is in both cases removed; in the one from the image itself, in the other from the paper. This accounts for the spotted appearance in the one case, and its absence in the other.

To test this theory, the following experiments were undertaken by the writer. A print was thoroughly washed, then immersed in a solution of lead nitrate, and again slightly washed. On applying the chloride of lime toning bath, the print quickly changed to a rich brown colour, and, after fixing, had all the qualities of a properly toned print. In this case the lead combined with the chlorine, and acted like the silver nitrate. Another toning bath, consisting of lime water and gold trichloride, was prepared. Two well-washed prints were immersed, and left respectively for three minutes and fifteen minutes; on the latter a slight deposit of gold was visible, and also a diminution in the depth of the print after fixing. With the former the print was less affected. Prints in which silver nitrate and lead nitrate were present both toned admirably, but rather too rapidly for safety. On examination a trace of hypochlorous acid was found in the toning solution. A slight addition

of chloride of lime was next made, and prints in which silver and lead nitrate were present were immersed in the solution : they toned gradually and regularly. This last experiment, which was confirmed by others, showed that the calcium hypochlorite contained in the chloride of lime acted as a retarder to the toning operation, as the chlorine contained in hypochlorous acid combined with the silver nitrate equally with that evolved from the precipitating gold. This manifestly would check the deposition of the gold.

Another toning solution used is one made with sodium acetate and gold. In practice it is found that toning takes place most regularly when the print has been previously well washed. On adding a solution of sodium acetate to silver nitrate, a sparingly soluble silver acetate and sodium nitrate are formed by double decomposition. If, then, the silver nitrate be present in the print, the greatest portion of the adjacent sodium acetate is decomposed, and sodium nitrate left in its place. The subchloride and oxide of silver both seem to be as readily attacked by chlorine as the silver acetate. Hence the chlorine, having nothing at hand to absorb it (sodium nitrate not being able to do so), attacks the silver of the print and produces the bleaching action already referred to. When all the free silver nitrate, however, is washed away, the conditions are changed ; the sodium acetate will absorb chlorine, and form a chloracetate and hydrochloric acid, as indicated in the following equation :



$$2AuCl_3 + NaC_2H_3O_2 = 2Au + NaC_2Cl_3O_2 + 3HCl$$

Eventually an evidence of this reaction may be traced in the fact that the solution becomes acid, and refuses to tone.

The foregoing experiments exemplify the following laws :

(1) That a neutral solution of the gold toning bath is necessary.

(2) That some active soluble chlorine absorbent must be present, either in the print or in the solution.

(3) That when the affinity of the absorbent for chlorine is violent its action must be retarded.

In considering any toning solution, these three qualifications must be taken into account, and if one of them be violated a perfect print must not be expected.

The theory of fixing prints is the same as already indicated, and need scarcely be touched upon. The reason why potassium cyanide cannot be usefully employed as a fixing agent has been already shown to be due to the fact that the organic oxide of silver is soluble in its solution. It must be strongly impressed upon the student that two forms of double hyposulphites of silver and sodium are formed, one of which is soluble and the other insoluble. The soluble form undergoes a change in light which renders it insoluble; hence fixing the print in daylight should be avoided.

When prints are immersed in a solution of sodium hyposulphite, a certain portion of this salt is combined with the double salt of silver formed. Every print immersed therefore leaves a smaller quantity of the uncombined sodium hyposulphite in solution; and since the double salt of silver and sodium is soluble in the uncombined hyposulphite, it follows that care must be taken not to fix too large an area of print in the same solution, otherwise the insoluble salt will be formed in the pictures. The effect of this is seen in the fading of prints. No amount of washing will eliminate this insoluble form. The acid vapours to be found in the air will decompose it, and cause a liberation of sulphur compounds, which gradually bleach the black portions of the image, and give the whites a jaundiced appearance.

Even where the soluble double hyposulphite has been formed, washing the prints in a thorough manner is essential for permanency, for any trace of it will decompose in a

similar manner, as will also the sodium hyposulphite itself. In the writer's opinion the prints should be immersed in two separate solutions of the sodium hyposulphite; the first will form the necessary soluble salt, and the latter will cause it almost entirely to disappear, all traces being subsequently eliminated by the washing water. Some American writers have proposed to shorten the washing of the print by a final immersion in a solution of iodine, tetrathionate being formed; the reaction would be as follows:



Sodium Hyposulphite + Iodine = Sodium Tetrathionate + Sodium Iodide

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

Both these salts are soluble in water, but less so than the sodium hyposulphite, and the tetrathionate appears to be more readily decomposed. If a silver compound be present with the hyposulphite, the same reaction apparently takes place, though an exact analysis of it has not yet been undertaken. The quality of the washing water is important —it should if possible be rain water, otherwise pure spring water, to which a little alkali should be added for the first washing. This renders the elimination of the soluble salts more complete.

The causes of instability in a print are as yet imperfectly recognised; and, owing to the want of chemical knowledge on the part of some photographers, the fading has assumed a more mysterious aspect than is warranted. Take the case of the acetate toning solution. It has been shown that it becomes acid,* and the prints are often taken direct from this bath to the hyposulphite solution. An acid immediately commences to decompose the latter, and fading necessarily results. Washing between each operation should be insisted upon, and then the chances of fading are reduced to a minimum.

It may be mentioned here that the writer has for some years fixed his silver prints with a 20 per cent. solution of

sulphite of soda. In this body there is no liability for sulphur to be liberated during the fixing operation ; all that can be liberated is sulphurous acid. Silver chloride and organic compounds of silver are soluble in the sulphite, but only to the extent of one-tenth of that to which they are soluble in the hyposulphite. Silver sulphite is formed, which is soluble in sodium sulphite, and this is readily soluble in water. It is too early as yet to state the permanency of prints so prepared, but there is every reason to believe them to be more stable than prints fixed in the ordinary manner.

CHAPTER XXII

MANIPULATIONS IN SILVER PRINTING

THE papers employed in silver printing are known as Saxe and Rive, the former being suitable for large pictures, whilst the latter are preferable for smaller sizes. The following formula may be used for the albumen solution with which to coat the paper :

Ammonium chloride . . .	10 grammes
Spirits of wine	15 c.c.
Water	135 c.c.
Albumen	450 c.c.

The first three are thoroughly mixed, and the albumen, derived from the whites of eggs, is gradually added to the solution. Perhaps the simplest way of effecting solution and perfect mixture is to half fill a bottle with the albumen, and then to add a fair supply of roughly powdered glass. Shaking the bottle will cause the flocculent matter to be broken up, and leave it in a state ready for filtering through sponge or well-washed tow. The paper, having been cut into sheets of convenient size, is floated on the fluid, contained in a dish, the hands grasping its two opposite corners. The convex surface of the paper thus formed is

first brought in contact with the solution. As the hands are drawn apart, the paper pushes out all air-bubbles before it, and at length lies in perfect contact with the solution. It is a wise precaution to take, however, to raise the paper from one corner, to make certain of the absence of all air-bubbles, and then to allow it to remain at rest on the solution for a minute. It is next removed, and hung on a line to dry, being held by a couple of American clips, or thrown over a stretched cord. This last plan is apt to cause markings, though it is probably necessary when large sheets of paper are manipulated, owing to their tendency to tear if only suspended by two corners. When dry the paper will not be flat, and should therefore be rolled or put away between

FIG. 39.



flat boards. When a print having a dull surface is required, the following formula is sometimes used :

Ammonium chloride . . .	6 grammes
Gelatine	·6 gramme
Water	300 c.c.

The gelatine is first dissolved in hot water, and then the remaining salt added. The paper is floated for three minutes on this solution.

Another mode of producing a dull surface, which is very effective, is to use resinised paper. The annexed formula is workable, and is due to Mr. H. Cooper, jun. :

Frankincense	1 gramme
Mastic	·8 gramme
Calcium chloride .	from ·5 to 1 gramme
Alcohol	45 c.c.

Good Rive paper is immersed in this solution for half a minute, after which it is ready for floating on a moderately strong sensitising bath.

The Sensitising Bath

When a paper is weakly salted, say, having half the amount of chloride given in the formula for albumenising paper, a weak sensitising bath is usually employed, whereas with paper strongly salted, or for the resinised paper, one somewhat stronger is necessary. The following formulæ will show what the extreme strengths of solution should be:

Silver nitrate	6 grammes
Water	100 c.c.

and

Silver nitrate	15 grammes
Water	100 c.c.

The paper is floated on either of these solutions in the manner given for albumenising paper, the time of contact varying from three minutes in hot to five minutes in cold weather. It should be removed slowly from the sensitising bath to prevent waste of solution, and when hung up to dry by an American clip in the dark room, the drainings should be collected by attaching a slip of blotting-paper to the bottom corner. It is always advisable to have one corner lower than the others, as the sensitising solution thus drains more equally away.

In order to preserve sensitised paper from coloration due to the decomposition of the organic salt of silver, it may be placed between sheets of blotting-paper impregnated with sodium carbonate. Ready sensitised paper is sold in the market, the discoloration being prevented, as a rule, by the addition of nitric acid in some form.

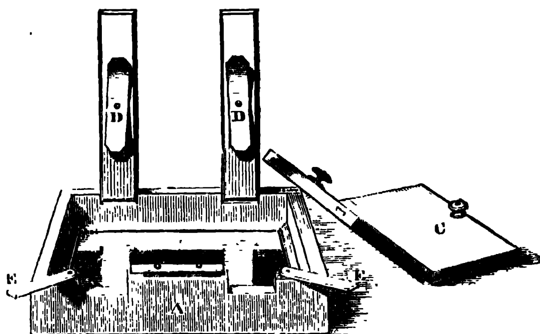
Printing the Picture

Printing operations are rarely carried on in the same temperature and state of atmospheric moisture as those in

which the paper is dried ; hence it is advisable to allow the paper to assume the conditions of the former before rigidly confining in the frame. The fact that paper expands in moist air at once shows that the dimensions of a photograph can never be relied upon as being accurate. Measurements have shown that a drawing, for instance, will vary as much as 1 per cent. in certain conditions of the atmosphere. The same remark applies to plans printed in the ordinary lithographic press ; the scale is never correct except under fixed conditions.

The negative should be placed in the printing frame

FIG. 40.



with the varnished side next the paper. A convenient form of frame, and one which is usually employed by photographers, is shown in the diagram (fig. 40). B is a sheet of thick plate-glass, which rests in a frame, A. The negative is placed on the glass, the sheet of paper over it, then a smooth felt pad, and over this a back, C, hinged in the centre. Two cross-bars, D D, to which are affixed springs, cause the back to press on the pad, and are held in position as shown by E E. The use of the hinged back is to allow the print to be examined when required. During such an examination one of the catches E is loosened, and the

portion of the picture beneath one half of the back can be inspected without any danger of the relative position of the paper and the negative being changed. The depth of the print is an important point to attend to. It must be remembered that much of the apparent vigour is lost in the subsequent operations of toning and fixing, and due allowance must be made for this. It requires considerable practice to judge correctly of the proper depth, and no fixed rule can be given, so much depending on the relative proportions of the chloride to the organic compound of silver, and on the nature of the toning bath. Much might be said about the artistic manipulation of prints, but it hardly enters into the scope of this work, though some hints will be given in the chapter on the picture.

Toning

The following toning baths may be considered standards:

I

Gold trichloride	·25 gramme
Chloride of lime	·25 gramme
Chalk (precipitated)	1 teaspoonful
Water	1 litre

The water should be boiling if the solution be required to be used at once, otherwise it should stand in an uncorked bottle for twenty-four hours.

II

Gold trichloride	·25 gramme
Sodium acetate	7 grammes
Water	1 litre

This should be mixed a day before being used. A very excellent toning bath for ready sensitised paper is as follows:

1.	Borax	24 grammes
	Water	1 litre
2.	Gold trichloride	·25 gramme
	Water	1 litre

The borax should be dissolved in the water with the aid of heat. Nos. 1 and 2 should be mixed in equal parts immediately before use to form the toning bath. Before toning, the solutions should be filtered in a clean dish, slightly warmed if the weather be cold. The prints are placed in water of about 15° C., and the washing continued as indicated in the last chapter, according to the toning bath employed. They are then immersed in the toning solution three or four at a time, and the dish is kept in constant motion, so as to allow an equal toning action throughout. It is likewise essential that no two prints should stick together, for the same reason. According to the colour of the print desired, so must the continuation of the toning action be regulated. If a rich chestnut brown be required, but very little apparent change in the colour of the print is necessary, whereas if an engraving black tone is sought, the action must be continued till the image is decidedly blue. It is not to be inferred that these rules are absolute in every case; so much depends on the sizing of the paper and on the amount of chloride present that they are not applicable in all cases, but with Saxe paper, prepared as given in the foregoing formulæ, they will hold good.

Fixing the Print

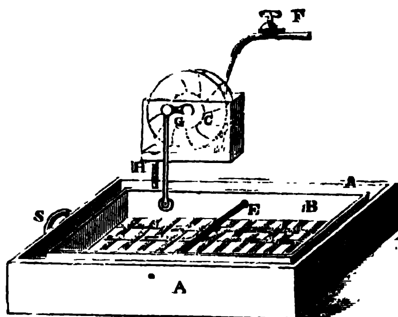
The fixing solution is made up as follows:

Sodium hyposulphite . . .	200 grammes
Water	1 litre.

Between toning and fixing it is essential that the prints should be well washed. The necessity of this may be understood by referring to p. 197. It has been sometimes recommended to acidify the washing water, but the proposer of this plan can have had no thought of the danger to the permanency of the prints which he thereby introduced; an acid at once begins the decomposition of the hyposulphite. The writer strongly urges the necessity of a distinctly alkaline

condition of this bath, and in practice he adds 50 c.c. of strong ammonium hydrate to it when fixing prints. Mr. J. Spiller was the first to point out the use of ammonium carbonate in the solution ; he showed that it dissolved out a certain compound left in the whites of the picture, which otherwise was insoluble, and which readily decomposed under atmospheric action. The pictures should be immersed in the solution for ten or fifteen minutes, the time varying according to the thickness of the paper ; they should then be washed (unless they be placed in a second solution of hyposulphite, as already suggested), rapidly at first and

FIG. 41.



afterwards more slowly. Perhaps the best way of eliminating the greater part of the hyposulphite is to place the prints in a large tub of water, which is kept in motion, and after five minutes' washing to place them in a smaller quantity of water. After this they may be removed to a washing trough, where the water will be changed several times an hour. The accompanying idea of a washing trough may prove useful (see fig. 41). It is one which was designed and is employed by Mr. England, and has answered well the purpose for which it is intended. A is a trough, at the side of which is a syphon, S, the inside leg reaching to within 2 or 3 millimetres of the bottom, the bend of

which is a little below the top of the trough. B is a cradle, pivoted on a rod, E, which passes through the sides of A, as shown. C is a water-wheel attached to the wall, on to which a gentle stream of water from the tap, F, plays. G is a small arm attached to the axle of the wheel, having a rod suspended from it, which is attached to the cradle, B. As the wheel slowly turns the rod is raised, and the prints are caused to move about in the water. The water runs into a trough through the pipe H, and when it reaches the top of the syphon pipe the trough gradually empties itself, leaving the prints on the gutta-percha strips which form the bottom of the cradle. It will be seen that the supply of water must always be rather less than that which the syphon is capable of carrying away. A useful addition to the trough is a horizontal pipe attached to the well of the wheel, moving from side to side by the motion of the wheel, and thus distributing the entering water over the surface of the prints by means of a fine rose. This prevents the chance of any of the prints getting surface-dry, which sometimes happens. In a trough of this description twelve hours suffice to ensure the total removal of the hyposulphite. Should this mode of washing be inapplicable, the prints may be placed in dishes, changing the water every quarter of an hour for the first hour, and every half-hour subsequently for six hours. If during this time they are well sponged twice or three times with a soft sponge, it will be found on applying one of the following tests that the hyposulphite is eliminated.

The first test is based on the reaction of iodine with sodium hyposulphite, shown at p. 198. Take a small piece of starch the size of a pea, powder it and boil it in 10 c.c. of water till a clear solution is obtained; add 5 c.c. of a saturated solution of iodine in alcohol to the clear liquid. A dark blue colour due to starch iodide will now be apparent. Drop 2 drops of the solution into two clean test-tubes, and fill up one with distilled water, and the other

with the water to be tested. A faint blue colour should be perceptible in the first test-tube, whilst the presence of hyposulphite in the other will be shown by the total absence of colour. The contents of the two solutions in the test-tubes can be best compared by placing a piece of white paper behind them and examining them by reflected light. The sodium hyposulphite may not be found in the washing water, yet a trace may remain in the prints. If a very weak solution of iodine be brushed across the back of a print, the absence of all colour will indicate the presence of the hyposulphite. One selected out of a batch of prints may thus be tested, though it is rarely necessary if the water indicates that the washing has been thoroughly effected.

The dishes that are used for holding the fixing solutions must in no case be employed for any other purpose. The material of which they are made should be, if possible, glass or porcelain, and never tin or zinc.

The defects in prints due to defective manipulation, and not to want of artistic skill, are but few in number. Red marks that repel the toning solution can usually be traced to contact with hot and moist fingers. A red tone after fixing is due to an insufficient deposit of gold, and a blue tone to an excessive deposit. The whites may appear yellow through the fixing solution being of insufficient strength, or through paper being used when the sensitive surface shows signs of discolouring through too long keeping. The general cause of the fading of prints has already been detailed.

CHAPTER XXIII

COLLODIO- AND GELATINO-CITRO-CHLORIDE PROCESSES

The processes are intended to be employed for printing on glass or paper, and for permanent silver prints nothing better can be desired. The following is a formula which is taken from the published process of Mr. Wharton Simpson:

No. 1.	Silver nitrate	. . . .	4 grammes
	Water	. . . . .	4 c.c.
,, 2.	Strontium chloride	. . .	4 grammes
	Alcohol	. . . . .	60 c.c.
,, 3.	Soda.	. . . .	1·5 gramme
	Alcohol	. . . . .	30 c.c.
,, 4.	Citric acid	. . . .	3 grammes
	Alcohol	. . . . .	30 c.c.

To every 50 c.c. of plain collodion 1 c.c. of No. 1 is added, being previously mixed with 2 c.c. of alcohol, in order to prevent precipitation of the pyroxyline. Next 2 c.c. of No. 2 are added with constant shaking, and ·5 c.c. of Nos. 3 and 4. In a quarter of an hour it is fit for use. It will be noted that there is a large excess of silver nitrate present. The amount necessary to combine with the strontium chloride is only ·29 c.c., and with the sodium citrate ·18 c.c. of silver nitrate; there is, therefore, present more than double the amount of silver nitrate necessary to combine with them. As already shown, this excess is requisite. In practice, particularly when printing on glass, it has been found very difficult to prevent the salts crystallising in the film whilst drying; and in order to overcome this source of annoyance, a method analogous to that of the washed bromide emulsion process may be employed. The above proportions of strontium chloride and sodium citrate may be kept, but the silver nitrate should be reduced to one-half. The plain collodion is made up with half

the solvents usually employed to dissolve the pyroxyline, and consequently only half the above quantity is used in mixing the collodio-chloride. After the emulsion is formed it is poured into a dish, allowed to set, well washed, dried, and then dissolved up in the proper proportions of solvents, in the alcohol of which ½ c.c. of the silver nitrate solution has previously been added. In this state the collodio-chloride contains the same necessary excess of silver nitrate, but the strontium and sodium nitrates are absent. This diminishes the risk of crystallisation taking place in the film, and with a certain class of pyroxyline this is entirely avoided. The silver citrate supplies the necessary organic matter by which a vigorous image is obtained.

If a glass plate has to be coated with the emulsion, the same directions as those given for coating emulsion plates should be followed, with the addition that it is well to dry the film before a fire, and to print whilst it is still warm. When a paper has to be coated more difficulty is found. The paper must be strongly sized; ordinary paper allows the collodion to penetrate through its pores, and a mealy appearance is sometimes the result. Arrowroot paper, supplied by most dealers in photographic materials, is perhaps the best kind. Obernetter, of Munich, uses an enamel paper as a support. A similar paper is prepared by coating ordinary paper with a strong solution of gelatine, in which barium sulphate, known as 'Mountain snow,' is mixed. When dry, this gives an impervious skin to the surface of the paper. The paper is pinned on to a board, the edges being turned up 2 or 3 millimetres, and at one corner a spout is formed, from which the collodion is poured off. The emulsion is now applied as if to a glass plate. Some operators find that by fuming the film with the vapour of ammonia, after thorough drying, increased vigour is imparted to the print. In any case this end may be attained by applying a solution of gallic acid and acetate of lead, together with a few drops of a solution of silver nitrate.

The print may be toned in any of the ordinary toning baths. Ammonium sulphocyanate and gold have been recommended, but the tones thus obtained vary greatly in richness.

For printing on glass a special printing frame has been designed, but this is not required if the precaution be taken to gum a strip of paper along the corresponding edges of the sensitive plate and of the negative. They may then be separated one from the other with the certainty that they will fall into their original position. The prints are fixed in sodium hyposulphite, made as under:

Sodium hyposulphite . . .	33 grammes
Water	1 litre

An immersion of eight minutes in this solution is sufficient.

A gelatino-citro-chloride emulsion, which was introduced by the author, may be made as follows:

1.	Sodium chloride	3·7 grammes
	Potassium citrate	1·8 gramme
	Water	50 c.c.
2.	Silver nitrate	11 grammes
	Water	50 c.c.
3.	Gelatine.	15 grammes
	Water	175 c.c.

Nos. 3 and 2 are mixed together, and then an emulsion formed in the usual way by adding No. 1. Sometimes it is found easier to emulsify if the sodium chloride and potassium citrate are kept separate, each in 25 c.c. of water. In this case the chloride emulsion is made first, and then the citrate added. The emulsion is squeezed into cold water, and slightly washed for a quarter of an hour. It is then drained and dissolved (see pp. 106 and 107) with the addition of 15 c.c. of alcohol. Should the emulsion appear granular, it is heated for ten minutes on a water-bath. Glass plates may be coated in the usual manner, or paper may be floated on it as in coating albumenised paper. Prints on such a paper possess great vigour. The image prints of a violet

tint by reflected light, and by transmitted light is of a deep chocolate. If fixed at once, the tint by reflected light is burnt-sienna colour. The following toning bath will yield good tones:

Ammonium sulphocyanate	7 grammes
Water	1 litre
Gold trichloride	·12 gramme

The print should after toning be transferred to another solution of ammonium sulphocyanate (12 grammes to 1 litre of water), where it should remain five or ten minutes. After this it is washed, and placed in a solution of sodium hyposulphite (see p. 204). It is finally washed and dried.

During the last ten years great changes have taken place in the practice of silver printing. Gelatino-chloride papers have been introduced by many of the plate and paper manufacturers under various trade names, such as solio, sylvio, &c., and are popularly known as P.O.P. (printing-out paper); these papers have to a large extent superseded the once popular albumen paper, though it is still doubtful whether any permanent advantage attends their use. The papers as bought will keep for a considerable time without discolouring, but they should be stored in such a way as to preserve them from damp and from the fumes of gas, otherwise much difficulty will be experienced in obtaining rich and uniform tones. The manipulation is much the same as with albumen paper, but fresh toning solution must be used for each batch of prints. The toning baths recommended for albumen paper may be used, and will generally yield good results; in working with a strange brand of paper it is advisable to employ the toning bath recommended by the maker.

CHAPTER XXIV

PRINTING WITH IRON AND URANIUM COMPOUNDS

THE majority of these processes are not very generally employed for the production of prints, but still they are useful for certain purposes, such as copying maps, plans, &c., by contact. An exception, however, is in the platinotype process, which is now very generally employed, and to which a separate chapter is allotted.

Printing Processes with Salts of Iron

Sir John Herschel investigated the relative sensitiveness of the different salts of iron, and came to the conclusion that the double citrate of iron and ammonia was more readily acted upon by light than any other, whilst after it came the double oxalate of iron and potassium. To produce the former salts, take a weighed quantity of ferrous sulphate, dissolve in water, and boil with nitric acid till it is thoroughly oxidised and in the ferric state; next precipitate with ammonium hydrate, and wash the ferric oxide in warm water to get rid of all the soluble salts. Transfer the washed oxide into a glass beaker and gradually add a solution of citric acid, and warm. When a small trace of ferric oxide remains undissolved, the addition of the citric acid should be stopped. Take the same amount of citric acid already added to the ferric oxide, and carefully neutralise it with ammonium hydrate, testing the operation with litmus paper. Then mix the two solutions together and evaporate to dryness over the water-bath, and when sufficiently concentrated allow the crystals of the double citrate of iron and ammonium to separate out. After carefully drying between blotting-paper they are ready for use. The double oxalate of iron and potassium may be

prepared in a similar manner. When required to render paper sensitive the following proportions should be taken :

Double citrate of iron and ammonium .	10 grammes
Water (distilled)	100 c.c.

This is applied to the paper with a brush, or else the paper may be floated on it. When dry it is exposed beneath a negative from a minute in bright sunshine to a quarter of an hour in diffused light, when it is ready for development, though the image will be barely visible. If a blue picture be required, all that is necessary is that the print should be immersed in a solution of potassium ferricyanide. After a few seconds the image will be found perfectly developed. A copious washing in water (in which a little citric acid has previously been dissolved for the first washing) will dissolve out all the soluble salts, and leave the blue image unchanged. The theory of this reaction has already been explained in chap. iv., and need not again be discussed. When pictures were developed by this method the process was called cyanotype by Sir J. Herschel.

Instead of developing with the potassium ferricyanide, the exposed paper may be immersed in a dilute and *neutral* solution of gold trichloride. The gold gradually deposits on the exposed portions and gives a purple image. This method of producing pictures on an iron salt has been called the chrysotype. The reduction of the gold follows from the fact that the *ferrous* salts are capable of reducing salts of gold to the metallic state when coming in contact with them in solution. In the case of pictures taken by means of the double *oxalate* of iron and ammonium, it is well to add to the gold solution a little neutral ammonium oxalate. The development in this case takes place very rapidly. To fix the pictures they should be immersed in water slightly acidified with hydrochloric acid, and then be thoroughly washed.

An exposed paper prepared with any double salt of iron

and ammonium may be developed by floating it on a solution of silver nitrate to which a trace of gallic acid and acetic acid have been added; the ferrous salt reduces the silver nitrate, and causes the metallic silver to deposit where the ferrous salt existed. The gallic acid subsequently causes a further reduction of the silver nitrate, and the first deposit of silver attracts a further deposit. An image is thus built up.

Founded on the same reaction pictures may be obtained by means of platinum tetrachloride, mercuric chloride, and potassium dichromate, &c., though greater exposure with these is necessary.

Another modification of the iron process described is the production of a positive from a positive. It is founded on the fact that potassium ferrocyanide forms an insoluble compound with a ferric salt and not with a ferrous salt. If, then, a ferric salt be acted upon by light it gets reduced to the *ferrous state*, and if the paper be floated on potassium ferrocyanide, on the part unacted upon by light a blue precipitate is formed, and on the part acted upon a slight stain of lighter blue. To prepare a paper which shall give clean prints it is usual to mix the iron salt with a solution of gum, and to develop with a mixture of ferro- and ferri-cyanides of potassium. Both the exposed and non-exposed parts of the paper are tinted blue, but the gum dissolves off from the portion of the paper exposed to light, carrying that portion of the blue colouring matter with it which was formed by the iron which was reduced to the ferrous state and which had combined with the potassium ferricyanide; thus leaving the part unacted upon by light behind as blue on a white ground. This process is useful for copying tracings, but the paper in this case must be placed in contact with the *back* of the tracings. In engineers' drawing-offices paper of this description has come into very general employment, as it can now be purchased of excellent quality.

About 1857 Salmon and Garnier brought out a process dependent on the fact that the ferrous salt resulting from ferric citrate is more hygroscopic than the ferric citrate itself. Paper coated with the ferric citrate is exposed, and then covered over by an impalpable powder, such as plumbago. The surface is then gently breathed upon, and more or less of the powder adheres, approximately in the inverse ratio of the amount of actinic light that has been allowed to fall on it. When sufficient intensity is secured the non-adherent powder is removed by a soft brush. The unaltered citrate is easily washed out of the film, leaving the powder image on the surface of the paper. Better results are obtained when sugar of milk or loaf sugar is mixed with the citrate. The process is not perfect, being defective where half-tones are required ; for the reproduction of engravings, however, it is excellent. It will be noticed that, to produce a *positive* picture, a transparent positive reversed as regards right and left must be employed.

Poitevin's Process with Ferric Chloride and Tartaric Acid

In Poitevin's process another property of a ferric salt is brought to bear, viz. the fact that it makes gelatine insoluble. A 6 per cent. solution of gelatine in water is prepared, with which is mixed any suitable pigment. Paper is floated on it whilst still warm. The paper now presents a uniformly coloured surface. To sensitise the paper it is immersed in a solution of

Ferric chloride	10 parts
Tartaric acid	3 parts
Water	100 parts

and after drying in the dark it is ready for exposure. When exposed to light, the gelatine, which was insoluble, becomes soluble in hot water. If, therefore, the paper be exposed beneath a positive (reversed as regards right and left), an image may be developed by simple immersion in hot water. The parts which are insoluble remain next the

paper; hence a perfect image may be developed with care. The student should compare this process with the autotype process (p. 224), and note the comparative advantages and disadvantages of the two. It seems to the writer that there is a possibility of a great future development of this process.

Printing with Uranium Salts

The usual salt of uranium employed for printing processes is the uranic nitrate, and, as has been indicated, this is reduced to the uranous state by the action of light in the presence of organic matter. The following may be taken as a good strength of solution:

Uranic nitrate	40 grammes
Distilled water	250 c.c.

The paper should be floated about eight minutes, as for sensitising paper in the silver bath. When dry it is ready for exposure, which is somewhat long. To produce a brown picture, float the exposed surface on the following:

Potassium ferricyanide . . .	1 gramme
Nitric acid	2 drops
Water	250 c.c.

In about five minutes the whole of the detail will be visible. After thoroughly washing in slightly acidulated water the image will be fixed.

To produce a grey picture, the exposed paper should be floated on

Silver nitrate	2 grammes
Water	40 c.c.
Acetic acid	3 or 4 drops

The image appears very rapidly, and attains full intensity if the exposure have been sufficiently long. If it be weak, a few drops of a saturated solution of gallic acid added to the above will produce the desired effect. Washing in water

will fix the picture, though care should be taken that no chlorides or carbonates are present in it. If any doubt exist as to their presence, sodium hyposulphite must be resorted to. The picture may be toned with gold, platinum, or other salts, as may be desired.

Uranium will also reduce the soluble salts of gold to the metallic state ; hence a picture may be developed with these.

A pleasing variety in these prints can be made by mixing with the uranic solution some ferric salt, and developing with the potassium ferricyanide. The resulting tone is richer and quite as permanent. Various other modifications have from time to time been made for the production of different shades of colour in the print.

CHAPTER XXV

THE PLATINOTYPE PROCESS

THE beautifu platinotype process is dependent on the reduction of a ferric salt to the ferrous state. Mr. Willis, to whom the discovery of this process is due, found that when a platinous salt, the chloro-platinite of potassium, was mixed with a ferric oxalate and then floated on a hot solution of neutral potassium oxalate, where light had acted, there the platinum salt was reduced to the metallic state. The following seems to be the reaction :

Ferric Oxalate becomes Ferrous Oxalate and Carbon Dioxide

$$Fe_2(C_2O_4)_3 = 2Fe(C_2O_4) + 2CO_2$$

When the hot solution of neutral potassium oxalate is applied, the ferrous oxalate is decomposed and the following reaction takes place :

Ferrous Oxalate and Chloro-platinite of Potassium become Ferric Oxalate,

$$6Fe(C_2O_4) + 3K_2PtCl_4 = 2Fe_2(C_2O_4)_3$$

Ferric Chloride Potassium Chloride and Platinum

$$Fe_2Cl_6 \quad 6KCl + 3Pt$$

The image formed is in one of the most stable substances known ; being unattacked by ordinary atmospheric influence, the pictures by this process may be considered to be permanent.

The paper used has to be sized to prevent the image sinking into the surface. Gelatine or arrowroot are the sizings which are most usually employed. For the latter size the following preparation answers : 10 grammes of arrowroot are rubbed up in a mortar with a little water, and gently poured into a litre of water which has been brought up to boiling-point. After the liquid has boiled a short time 200 c.c. methylated spirit are added, and the solution is filtered. The solution should be poured into a dish slightly larger than the paper to be employed. The sheets are drawn into the solution, taking care that no air-bells form. They should be left in it two or three minutes, when they are taken out and hung up in clips to dry.

The following solutions are prepared according to the directions given by Pizzighelli and Hubl :

No. 1.	Ferric oxalate	8 grammes
	Oxalic acid	·5 gramme
	Water	26 c.c.

This solution must be kept absolutely in the dark.

No. 2.	Chloro-platinite of potassium	8 grammes
	Water	50 c.c.

When preparing the sensitising solution the following is the mixture :

No. 1	22 parts
No. 2	24 parts
Water	4 parts

The two experimenters we have quoted add a certain proportion of a solution of chlorate of potash to this to give more or less deep blacks, but the above may be taken as the normal solution.

The coating of the paper takes place in a feeble light.

Yellow light is the best, but it is hard to see the colour of the solution. The paper should be pinned by the corners on a smooth board, and the sensitising solution applied with a piece of flannel enclosing a pledget of cotton wool. For 1,000 c. square about 3 c.c. of solution is required. This quantity should be poured in the middle of the sheet of paper, and be immediately spread over with a circular motion. The rubbing should be very gentle, and should be continued until the coating is as uniform as possible. The paper must be dried in from five to ten minutes, and it is of the utmost importance that it should be thoroughly dried. If the paper take too long in drying, the image will appear sunken, and if too short a time the platinum will wash off during development.

When the paper is placed on a negative it should be backed with vulcanised india-rubber, or well-waxed paper, to prevent the access of any moisture to it during printing. The time of exposure varies upwards from two-thirds of that necessary to give to a silver print of the same subject: it depends on the sensitiveness of the material and the mode of development. The process works best with negatives of good density and gradation.

To develop the print the following solution should be made:

Potassium oxalate (neutral) . .	300 grammes
Water	1 litre

The solution should be brought to a temperature of between 77°C. and 85°C., and is conveniently kept heated in an enamelled iron dish over a source of heat. The developing solutions may be used over and over again, by decanting from any green crystals which may appear on cooling. The development takes place by floating the paper on the solution, or it may be dragged over its surface.

The print is fixed and washed by passing the print into a solution of hydrochloric acid (1 part to 60 of water) immediately after developing, where it should remain, face

downwards, for ten minutes. It should then be passed into another bath of the same strength for the same time, and finally be washed for a quarter of an hour in three or four changes of water.

With a feeble negative the temperature of the developing bath may with advantage be lowered to 60°, or if a print be much over-exposed the same artifice may be resorted to.

Platinum prints in a wet state appear more brilliant and lighter than they do when dry, and this must be taken into account.

The Platinotype Company issue paper which gives tones approaching sepia, with which they issue special instructions. It is believed that this tone is dependent on the use of a mercury salt in combination with the platinum.

Platinum paper, before and after printing, should be stored in boxes containing calcium chloride. Such boxes, of a very convenient form, are supplied by the Platinotype Company. The chloride may be dried from time to time over a Bunsen burner.

Cold Bath Process

In 1892 Mr. Willis introduced a modification of the process by which the prints would be developed with a cold developer. There is some small difference in the preparation of the paper, but what that is is more or less a secret. The image has to be printed rather deeper than with the hot development; all but the faintest outlines should be visible. The printed paper is floated face downwards upon a 1 to 6 solution of neutral potassium oxalate, though the strength is not very material, the action of a weaker solution being to render the development slower. A solution rendered slightly acid with oxalic acid will give cold tones, while the addition of sodium carbonate sufficient to cause litmus paper to turn blue will give warmer tones.

The Platinotype Company have a developing salt which gives coldish but black tones. The development takes place by floating, and when moistened the print may be laid on a sheet of glass face upwards and watched till the desired strength of image is attained, when it should be immersed at once in the clearing bath (HCl) to check further action. Local variation in the strength of a print may be obtained by the adoption of glycerine development. The print to be developed is laid on a sheet of glass and the whole surface brushed over with glycerine by a flat camel-hair brush. Cups containing a strong solution of developer, and the same with glycerine, should be at hand. A mop-brush of suitable size is dipped in the neat developer and passed over those parts which require full strength. When these are correct the other parts are painted over with the glycerine-diluted developer, the developers on the various parts being worked together to avoid harsh or irregular action. The print by this means may be rendered artistic; but a clear perception of what is required, with skill in using the brush, is necessary. The subsequent operations are the same as before. The use of the glycerine is to check the excessive action of the developer; and as the salts are not actually soluble in it, this is effectual for the same reason that it is so in the wet-plate developer.

CHAPTER XXVI

PRINTING WITH CHROMIUM SALTS

As already pointed out in chap. iv., the dichromates are acted upon by light in the presence of organic matter, and the result is to render such organic matter insoluble in, and non-absorbent of, water. The following experiments may be undertaken.

1st. Let albumenised paper be prepared such as is described at p. 199, preferably omitting the chlorides &c.,

and employing only the albumen, and float it on a 6 per cent. solution of potassium dichromate. If the student exposes one of these pieces of paper in a dried state beneath a negative or an engraving, he will find that on soaking it in cold water all the albumen that has been acted upon by light will remain insoluble, whilst that protected will readily dissolve. Three or four small pieces of gelatinised paper may next be prepared by brushing over the paper a viscous solution of gelatine, in which is dissolved the above proportion of the dichromate. When dry, they may be fully exposed to light beneath negatives of line engravings. On immersing one of them in cold water, it will be noticed that the protected parts immediately begin to swell, through the absorption of water, whilst those portions unprotected remain unchanged. On immersing another sheet in hot water, the protected gelatine will dissolve away entirely, whilst the rest will remain firmly attached to the surface of the paper. Another sheet of exposed gelatinised paper may next be brushed over with thin, greasy, lithographic ink, and after soaking in cold water, a wet sponge may be applied to remove all the ink that will come away. It will be found that the non-absorbent parts retain the ink, whilst the latter reject it. If portions have been only partially protected, as in the case of what is called a half-tone negative, the ink will be found to adhere thinly on them, owing to the gelatine having become only partially non-absorbent.

One of the earliest processes in which a dichromate was used was that due to Salmon and Garnier, and is similar in principle to the powder processes which are to be described Poitevin and Talbot were, however, first in the field with a practicable application of it.

Swan's process was the first commercially successful, and a brief outline of it may not be uninteresting, as it is still worked by Braun of Dornach. The organic matter employed is gelatine, and it is applied to the surface of paper, after having been coloured with some unalterable

pigment, such as lampblack, and sensitised with ammonium dichromate. The prepared paper is next exposed beneath a negative till it is judged sufficiently printed.

The student must now try to realise the work that the light has been performing. Those parts of the gelatine next the negative will have become insoluble to a depth corresponding to the intensity of light entering, and, as there will be but little of the negative which will not allow some light to pass through, it may be considered that the whole of the exterior surface of the gelatine has become insoluble, whilst the soluble portions remain enclosed between the insoluble layer and the surface of the paper. If such a print were immersed in hot water to dissolve away the unaltered gelatine, the viscid solution would remain imprisoned, and no development of the image would be possible. This difficulty Swan overcame by cementing the insoluble surface to paper by a solution of india-rubber. On immersion in hot water the original paper easily strips off, leaving the water free access to the soluble gelatine. When this is completely dissolved away, an image in pigmented gelatine remains on the india-rubbered paper, though reversed as regards left and right. This defect, again, was overcome in one of two ways—either by using a negative reversed as regards left and right, or by the following procedure. Another piece of paper, coated with starch or gelatine, was applied to the image, and allowed to dry in contact. The india-rubbered paper was then moistened with benzene or some other india-rubber solvent, and detached.

It will be well to draw the student's attention to the reason why the portions of the film of gelatine become insoluble to depths corresponding to the intensity of light, instead of becoming only partially insoluble through their whole depth. The light that is chiefly effective in causing the reduction of the dichromate is the blue. Now, since the dichromate is of an orange colour, it is evident that an absorption of the blue will take place, and experiment

has shown that a small thickness of gelatine coloured by it will prevent any effective ray being transmitted. In order to cause the reduction of the chromium compound, the amplitude, multiplied by the number of the waves, must be of a certain constant numerical value; if the product falls short of this constant no change will be effected. On this assumption it will be readily seen that insolubility will take place only to certain depths, depending on the length of exposure and intensity of the light. At the same time it will be seen that it does not necessarily follow that the *whole* of the gelatine or other organic body becomes insoluble to that depth, but that the ratio of soluble to insoluble matter increases as the depth becomes greater. This last point is important, for it seems that the photo-mechanical printing processes are really dependent on it.

In order to obtain perfection in prints formed in gelatine, the image should be dark-coloured and transparent or translucent, in order that the minutest difference in shades may be observable; in other words, the white ground of the picture must play its part in this as in silver printing.

J. R. Johnson was the first to improve upon Swan's process; he found that the insoluble gelatine could be caused by atmospheric pressure to adhere to any impervious surface. This he effected in the following ingenious way. The undeveloped picture, printed in the usual manner on gelatinised paper, was immersed in cold water, and allowed to absorb a certain quantity of the fluid, causing the unaltered gelatine to swell slightly. Immediately that the curling of the paper in the water showed that sufficient fluid had been imbibed, he brought the surface of the gelatine and a metal plate nearly in contact, a thin layer of water being allowed to separate them. This water he squeezed out, and, the gelatine continuing to swell owing to the fluid remaining in the pores of the paper, a partial vacuum was created between the two surfaces, and the insoluble gelatine was found to adhere firmly to the metal

plate. When the picture, so held, was immersed in hot water the paper backing could be stripped off, and development took place on the temporary metallic support. Gelatinised paper applied to the image could then be employed as a final support. In practice it was found that this method of development was liable to cause a loss of sharpness in the image, owing to the tension of the gelatine. To overcome this, Mr. Sawyer, of the Autotype Company, prepares an insoluble gelatinised paper support, to which the gelatinised paper is caused to adhere by the same means. In this case the support will expand with the image, and the want of sharpness is thus overcome.

It would be impracticable to recount all the various suggestions that have been made for the improvement of the gelatine process. Much ingenuity has been brought to bear on it, and it seems now to have arrived at a state bordering on perfection. Many of the improvements in it have been in the past patented, and thus the working of the process has been in a measure restricted to the licensees of the Autotype Company, to whom most of these patents have been assigned. The Autotype Company and other firms now supply the materials to all, and the process can be worked without a licence. The manipulation of the autotype process will be described, as it is that which has gained the greatest success.

In regard to the insolubility of dichromated gelatine after exposure to light, a remarkable fact was noticed by the writer. It was found that where the insolubility of the gelatine caused by light had once commenced, it continued in the dark, and that the action was further increased by exposure to what would ordinarily be non-actinic light. This remarkable property has been utilised in the autotype process to diminish exposure; and Marion, of Paris, likewise took advantage of it in a process known as Mariotype. An outline of this process is as follows: A paper is coated with gelatine, rendered insoluble by alum, and

sensitive by potassium dichromate. It is exposed beneath a negative; and a sheet of gelatinised and pigmented paper, which has also been impregnated with potassium dichromate, is brought in contact with it in an unexposed state. The two are kept beneath pressure in the dark for eight or ten hours, and are then withdrawn. The action set up in the impregnated paper by the light is communicated to the other coloured gelatine, and, as it starts from the bottom surface of this towards the top, the soluble portions are exposed to the solvent action of water, when the paper support is removed. The development takes place in the ordinary manner, and the image is not reversed as regards right and left. The process is not practised to any extent, but is a curious example of a catalectic action started by the impact of light.

All gelatine which has been long in contact with a dichromate, when dried becomes insoluble after a time without any exposure to light having taken place. The probable cause of this has been shown at p. 32. In hot climates the drawbacks to the use of gelatine in any form are that the ordinary temperature of the water is such as to render it liable not to set, but to remain in solution, and if dried it rapidly becomes insoluble. With care, of course, the want of setting power may be avoided, but there is no doubt that the difficulties of working this process in the tropics are far greater than in a temperate climate such as that of England.

The paper when coated with gelatine and pigment is technically termed carbon tissue, and as such it will be referred to.

Since the original patent of Swan many improvements in the manufacture of the tissue have been made, and the different substances added to the gelatine are only partially known to the public. The Autotype Company and other firms supply the tissue at a reasonable rate, and an amateur cannot do better than procure the needful supply from them

in preference to making it himself. Should he determine to make it himself, however, the following solution should be prepared:

Nelson's No. 2 flake gelatine . .	100 grammes
Sugar (brown)	10 grammes
Honey soap	10 grammes
Glycerine	20 c.c.
Water	490 c.c.

Pigment of a permanent nature is finely ground, and incorporated with a little warm gelatine and glycerine, and then mixed into the above. Aniline dyes may be employed, though some are apt to render the film insoluble, as are also certain kinds of pigments. There are two ways of applying this gelatine solution to paper. A fixed quantity may be taken in a measure and applied to paper which has previously been soaked in warm water, all excess of moisture being blotted off on blotting-paper. The paper in this case is placed on a carefully levelled glass plate, and the proper quantity of fluid poured on and distributed evenly over the surface by means of a glass rod. In cold weather the gelatine will set almost at once, and when firm the paper is hung up to dry. In warm weather iced water may be caused to come in contact with the bottom surface of the glass plate, which will cause the setting to take place rapidly. Rapidity in setting and drying is conducive to sensitiveness, and hence must not be overlooked. The next method is simpler, perhaps, and almost as effective.

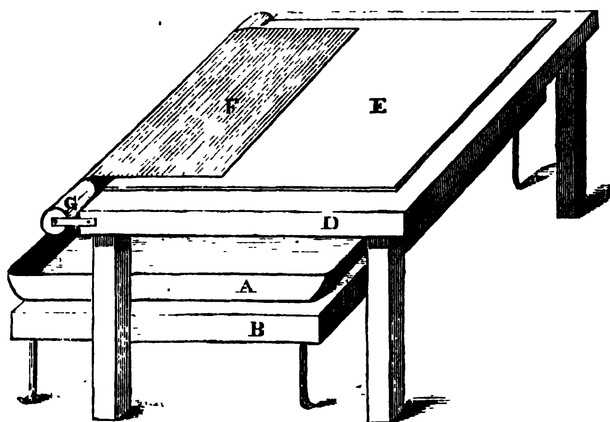
A porcelain or other dish, A (fig. 42), is placed on a hot-water tin, B, the water being kept at boiling-point by a lamp or Bunsen burner. Over the dish is placed a level table, D, at one end of which is a roller, C, that is on a level with the top surface of a glass, E, placed on the table, D. The paper, F, is floated on the warm gelatine solution contained in the dish, drawn through it, seized by the hands and drawn over the roller on to the plate, E, where it is allowed to remain till the gelatine is well set, after which it is hung

up by clips to dry. The dish has to be removed each time that paper is floated; if B be lengthened, the dish can be run backwards and forwards in a very simple manner.

In making the tissue a great point is the selection of the paper. It will be found advantageous to use rather a porous kind, not over-sized. A wash of ammonium hydrate improves it, as all grease is thereby removed.

Another point to be attended to is the temperature of the gelatine solution. If raised too high, the coating given

Fig. 42.



to the paper becomes irregular. Much practice is required before paper can be evenly coated, and it will even then probably be found inferior to that obtained from the manufacturers. Air-bubbles are a constant source of annoyance and are with difficulty avoided; the surface should be well skimmed from them before paper is floated.

The tissue when dry is improved by being rolled in a copperplate press, though it is not essential if the glycerine added have been sufficient to cause it to remain somewhat limp. One coating is generally sufficient, though if the

white of the paper show through the gelatine and pigment it will be necessary to give it a second coating in the same manner as before.

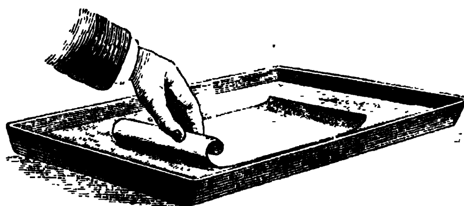
Should it be required to sensitise the gelatine at once, 40 grammes of potassium dichromate should be added to the above.

Whether the tissue be home-made, or be supplied by the Autotype Company, it can be sensitised in a solution of

Potassium dichromate . . .	50 grammes
Water	1 litre

This solution should not contain free acid, as if it does the tissue is liable to become insoluble. This fact has been

Fig. 43.



utilised by Dr. Monckhoven in his method of preparing carbon tissue. In order to float the tissue on the above solution, a dish somewhat larger than the piece to be sensitised is used; and it is coiled up in a small roll, with the gelatinised surface outside. The extreme end of the tissue forming the roll is turned up for a centimetre. In this form the tissue acts as a spring, and will unroll itself if allowed to do so. Advantage is taken of this. The turned-up end is brought to one side of the dish and dropped on the solution. The hand grasping the roll is gradually unloosed, and the tissue, uncoiling itself, pushes the end which first touched the solution to the farther side of the dish, and lies flat on the solution, all chance of air-bubbles clinging to it being thus avoided.

After floating for three minutes, the turned-up end is pinned to a lath, by which it is hung up to dry. The drying-room should be well ventilated, and have a constant current of dry air circulating through it in order to cause rapid drying, which is so favourable for sensitiveness. When quite dry the paper is exposed under a negative in the ordinary manner, taking the precaution, however, to leave a small portion at the external edges of the tissue not exposed to light, since this gives greater certainty of adhesion to the metal plate, or other impervious surface, in the subsequent operations. A mask of brown paper placed over the negative effects this. Owing to the colour of the pigment no change of appearance in the tissue will be noticed if examined after exposure. It is therefore necessary to resort to an actinometer in order to judge of the exposure. The simplest form is chloride of silver paper exposed in the same light as the tissue through a small aperture surrounded by a medium tint of the same hue as that which the chloride takes after moderate exposure. Two to three such tints may be required.

By adopting the plan of under-exposing, and leaving in the dark, or in non-actinic light, as explained at p. 225, the exposure, of course, can be materially reduced.

When in a developable state a shallow tin or other dish is filled with water, and a finely-mulled zinc plate is placed at the bottom of it. The plate must have been previously treated with what is known as waxing composition, made as follows:

Beeswax	3 parts
Yellow resin	3 parts
Oil of turpentine	160 parts

These proportions are not absolute, as the composition of the beeswax varies. 'The resin must be added to the beeswax in such proportions that the gelatine film will remain on the plate without cracking or peeling, even when dried in a hot room, but at the same time will leave the

plate readily (when the applied transfer paper has become dry) without the application of any force.' The plate is first rubbed with a piece of flannel, on which has been smeared a small quantity of the fatty body. All excess of wax, except a very fine layer, which persistently adheres, must be removed by polishing. It is not necessary to wax the plate each time a print is removed, but this must be done whenever the gelatine image shows a tendency to stick to the zinc plate during transference to the permanent support. The plates are freed from dirt and greasy matter by the application of a little turpentine, ammonia, or potash.

To attach the gelatine surface to the zinc plate the tissue is immersed face downwards in the water in the dish, and as soon as it begins to curl *upwards*, the zinc plate is lifted out of the water, carrying between it and the surface of the gelatine a layer of water. The plate is then placed on a small low stool (slightly smaller than the zinc plate), and the excess of water squeezed out by means of a squeegee. The squeegee is shown in fig. 44. It consists of a flat bar of wood, into which is let a piece of india-rubber about half a centimetre thick and two centimetres broad. When all the superfluous water is thus expelled,[1] the gelatine film is allowed two or three times to expand, and is then placed in warm water of a temperature of about 40°C.

Fig. 44.

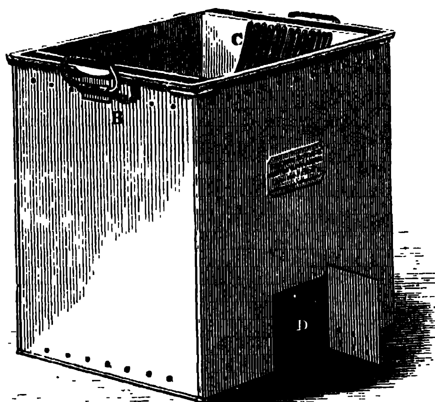


Fig. 45 shows the developing trough as supplied by the Autotype Company, and it certainly is very convenient for the purpose. A is a trough, fitting into a case B, leaving a space D below, in which a Bunsen burner can be placed, in order to heat the water in A; along the sides of A are grooves, C C, into which the zinc plates slide.

[1] A certain amount of dexterity is required to prevent the paper cockling at the edges; the india-rubber of the squeegee must be brought to bear with considerable pressure on to the surface of the paper, and the strokes made with it should commence from the centre and finish towards the ends.

After half a minute the paper can be removed from the gelatine, and after the water has had free access to it the image begins to develop rapidly, particularly if the plates be moved vertically in the trough. When all the soluble portion is dissolved away, the picture is washed in cold water, and dipped for a second or two in a weak solution of alum and water, and put aside in a rack to dry. Some operators prefer to use a deep dish in which to develop, and doubtless the development is equally readily executed by so doing, but only pictures of a total area less than that of the

FIG. 45.



dish can be developed at one time, whereas with the trough arrangement as many as a dozen pictures can be put in hand at once. For an amateur this is not a matter of great importance.

When the gelatine image is dried, a piece of transfer paper (which is paper coated with gelatine subsequently rendered insoluble in water by alum or other such body) is placed in water of about 60°C., and softened. The picture on the zinc plate is placed in a dish of cold water, and the softened transfer paper is applied to it in the same manner

as was adopted for causing the undeveloped gelatine image to adhere to the zinc plate.

After drying, the picture will peel off from the plate and adhere to the transfer paper. The carbon print is then complete.

The same manipulations, with a few evident modifications, are necessary when the temporary support is pliable.

When a reversed negative is employed, the image may be developed on the final support.

Gum-bichromate Process

During the last few years a revival of a process invented by John Pouncey about the year 1859 has taken place. At that time the process did not receive much support, but during the last six or seven years has attained a certain amount of popularity. In 1892 M. Artigue brought out a paper under the name of 'Carbon Velours,' coated with a deposit of pigment held in position by a colloid substance. The paper is sensitised by floating upon a solution of potassium bichromate; it is then dried in the dark, and printed upon from a negative in the usual manner, an actinometer of some sort being necessary to gauge the exposure.

Development is effected by first soaking the print for a few minutes in cold water, and afterwards by treating it with a mixture of sawdust and water. The abrading action of the fine sawdust speedily removes the pigment from those portions of the print not acted upon by light. Considerable care must be exercised during the various operations not to damage the delicate surface.

Soon after the introduction of the Artigue paper, M. R. Demachy and others coated paper in the Pouncey method with gum arabic, potassium bichromate, and pigment, the prints being developed in a manner similar to the Artigue paper.

Various methods of preparing the paper have been suggested; the following will yield good results.

A paper should be chosen in which the potassium

bichromate dries to a deep orange tint, if it does not allow the pigmented gum to become too intimately associated with the fibre of the paper.

The paper is first saturated with a 10 per cent. solution of potassium bichromate and dried in the dark. Four parts of the best Soudan gum acacia (in tears, not in powder) are dissolved in ten parts of water. Half a fluid ounce of the gum solution is taken, diluted with half an ounce of water, and incorporated with a suitable pigment—vegetable black, red and yellow ochre, burnt sienna, and burnt umber are all useful. Twelve grains of vegetable black are placed on a marble slab, and a few drops of the gum solution added and well worked up with a palette knife, the remainder of the half-ounce of gum being added by degrees. The pigmented solution is then spread over the paper with a 2-inch bear's-hair brush, and the coating equalised with a badger softener. The exact amount of pigment in the gum solution must be varied to suit different types of negatives.

If the paper has been correctly prepared, and a slip of it before printing is laid face downwards on cold water, the pigment should drop from the surface or should do so with a slight laving with cold water. The above method is that employed by Mr. James Packham.

The Ozotype Process

This process is the invention of Mr. T. Manly. A sheet of paper is sensitised by brushing over it a solution containing bichromate of potassium and a manganous salt; the solution is supplied by the patentees. The paper is dried in the dark and keeps indefinitely. Upon the paper so prepared the print is made: the image appears brown upon a yellow ground, and is washed in two or three changes of water. After drying, the print, together with a sheet of carbon tissue, is immersed in a solution of

Water	1,000 c.c.
Glacial acetic acid	2 to 5 c.c.
Hydrokinone	½ to 2 grammes

and are brought out, squeegeed into close contact, and dried.

Development is the same as with ordinary carbon process, except that the print should be soaked in cold water for from half an hour to one hour before being transferred to warm water. The manganese and chromium salts which compose the first image cause the gelatine with which the pigment is incorporated to become insoluble, thus bringing about the results which are effected in the older process by the direct action of light. If the paper chosen is not heavily sized it should be coated with a thin layer of gelatine or fish glue. No safe edge is required, and the process has the advantage of giving a non-reversed print.

CHAPTER XXVII

WILLIS'S ANILINE PROCESS

WILLIS's aniline process may next be briefly described. It is dependent on the action of dichromates on organic matter, though the printed image is given colour by means of aniline. Sized paper is floated in potassium dichromate, to which a little phosphoric acid has been added. It is then exposed beneath a transparent or translucent positive, such as a plan or map, and when the image is perfectly visible, it is exposed to the action of aniline vapour. Aniline salts have the property of striking a green, black, or reddish colour when brought in contact with acidified dichromates; hence these parts which have not been exposed to light, or have been shielded from it (as is the case with the lines of the positive print), are deeply coloured, the rest of the paper remaining of the faint colour due to the reduced chromium oxide. In developing these prints, aniline is dissolved in spirits of wine, and the mixed vapours are allowed to come in contact with the print. It will at

once be evident what an extremely valuable process this is for copying engravings, plans, and tracings. All that is required is a sensitising solution, a sheet of glass to place over the plan &c. (which, when exposed, should have its back in contact with the sensitive paper) to keep them in contact, and the sensitised paper. A rough box with a lid, on which can be stretched the printed paper, a basin to contain the aniline solution, and a spirit lamp to warm it, complete the outfit.

The prints can be washed, and are then tolerably permanent.

This process was patented by the inventor, Mr. W. Willis, the father of the inventor of the platinotype process. Whether in the face of the many other processes to effect the same object the aniline process will be worked is a matter of conjecture. There are various modifications of this method of printing by using coloured aniline dyes, such as rosaniline. For some purposes they are useful, but as a rule they are better for the reproduction of subjects executed in line than for half-tone negatives.

The Powder Process

Reference has already been made to Salmon and Garnier's process, in which originally salts of iron were employed to sensitise gelatine, the development being effected by the application of plumbago, or other impalpable powder. The dichromates subsequently were found to answer better than the ferric salts, the development of the prints being somewhat more easy with them. A mixture of gum arabic, sugar, and a little glycerine, together with a sensitising solution of potassium dichromate, is prepared and poured over a glass plate, or other impervious surface, and allowed to dry in a warm temperature. The plate thus prepared is at once exposed for a few minutes beneath a transparent positive and withdrawn. Those parts acted upon by light will be found to be hygroscopic in the ratio

of the time of exposure and intensity of the light. Any impalpable powder brushed over the plate will now be found to adhere to these hygroscopic parts in proportion to the moisture which they hold. Hence a positive, reversed as regards left and right, will result. When the image is developed it is coated with collodion, and can then be transferred to paper &c. in an unreversed position. The soluble dichromate will be washed out during the process of transferring. This process is sometimes employed for obtaining images which can be burnt in on glass or enamels. For those who wish to try the process the following formula for the sensitive compound will be found efficient. It is due to Obernetter, of Munich:

Dextrine	4 parts
White sugar	5 parts
Ammonium dichromate	2 parts
Glycerine	2 to 8 drops for every 100 c.c. of water
Water	96 parts

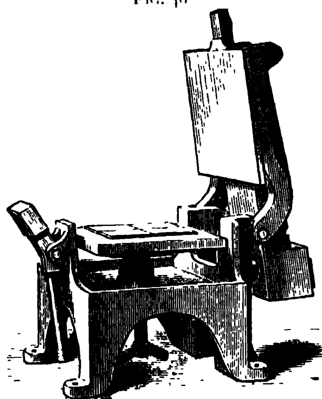
It is sometimes recommended to give the glass plate a preliminary coating of plain collodion. The powder must be very gently applied with a cotton-wool brush or fine camel's-hair brush.

Woodburytype

The Woodburytype process is an exceedingly ingenious method of obtaining a mould of a gelatine print, from which other prints may be obtained. A rather thick film of sensitive gelatine is prepared, resting on a tough film of collodion. This is placed beneath a negative, the collodion side being next the image. It is then exposed to light proceeding from a point, or to sunlight, arranged in such a manner that it always receives the rays in one direction. Uncontrolled diffused light will not do, as, owing to the thickness of the gelatine, the image on development would be ill-defined. When sufficiently printed, the gelatine picture is developed as if it were an autotype print, present-

ing the image in considerable relief. When dried, the gelatine picture is placed on a perfectly flat metal plate, and a sheet of soft metal (lead, for instance) is pressed on it by means of an hydraulic press. This latter presenting an exact mould of the former, is then placed in a press made as in accompanying figure. Gelatine is next dissolved in hot water and fine pigment or permanent dye added to it, and the viscous solution thus prepared is poured on to the mould. Paper of a very even texture, and which has been strongly sized, is placed on the top of the pool of liquid gelatine, and the top plate of the press, hinged as shown in fig. 46, is brought down on to the mould and firmly locked by the catch, also shown in the same figure, squeezing out the superfluous gelatine. When it is judged that the gelatine has set (which it soon does, owing to its contiguity to a mass of cold metal), the top is raised and the paper, which now bears the picture, is detached. The print is immersed in a solution of alum to render the picture insoluble.

FIG. 46



The top plate, which is of glass, must be a perfect plane, otherwise the liquid gelatine will not be squeezed out from the portions that are to remain white, and the print will be uneven and mottled. The great relief of the original image is necessary in order to give sufficient intensity to the reproduction, for it must be recollected that the gelatine solution, filling even the greatest depths of the mould, will present but a thin layer on drying. If the

mould were obtained from an ordinary gelatine print there would not be sufficient depth of colour properly to represent the various gradations of shade. The pictures obtained by this process are presumably permanent, and can be produced at a cost but little in excess of the gelatine solution and the paper employed. As can be understood, there are difficulties in the way of producing any large surface which should be represented by pure white, since, however homogeneous a paper may be, it is invariably slightly thicker in some parts than others, and this prevents the glass plate attached to the lid of the press from fulfilling its functions in an absolutely perfect manner.

CHAPTER XXVIII

PHOTO-LITHOGRAPHIC TRANSFERS

ANOTHER process, to which reference must be made, is that perfected by Colonel De C. Scott, R.E., and Sir Henry James, late Director of the Ordnance Survey of Great Britain. It also is dependent on the *insolubility* of gelatine when treated with a dichromate and exposed to light. It will be described in detail, as it is capable of producing prints in printer's ink, as well as in ink suitable to give a transfer on to zinc or stone. From such transferred prints the original drawing can be reproduced by ordinary surface printing. It may be well to notice the requisites for these transferable prints. First, the image should be made in an ink which is readily held by a lithographic stone or mulled zinc plate. Secondly, it must be capable of a fair amount of resistance to pressure ; that is, it must be tolerably hard and cohesive, otherwise the act of passing a paper holding the image through a lithographic press would cause a spreading of the ink, and a consequent want of sharpness in all the impressions taken from the stone. Thirdly, the

ink must be of such a quality that a very thin coating is sufficient to leave a sharp and firm impression on the stone or zinc plate. Fourthly, the paper on which the image is developed must be tough, and not easily torn or stretched. These requisites are fulfilled if the following directions are attended to. The best paper to select is that known as bank post paper, which is not highly sized. If it be, the sizing should be removed by immersion in boiling water, previous to coating it with the gelatine solution. The solution is prepared according to this formula :

Potassium dichromate . . .	44 grammes
Gelatine	44 to 66 grammes
Glycerine	2 c.c.
Water	1 litre

The varying quantity of gelatine is due to the fact that some gelatines give much more body to the solution than others. Thus, if soft gelatine be employed it has been found in the writer's experience that the larger quantity will be necessary, whilst if the harder qualities of gelatine be employed the smaller quantity will usually suffice. The gelatine is of course thoroughly softened in half the above quantity of water, and then the remaining half, in which the dichromate has been dissolved, is added in a boiling state. The solution is poured into a dish, and placed over the hot-water tin, as described at p. 227. A sheet of paper of the proper size is floated on it for three minutes, and then hung up by two corners to dry. This causes the coating to be thicker at the bottom corners than the top, to avoid which resort may be had to the artifice shown in the figure, p. 228. In any case a second coating is required, and this is given in a similar manner. If the paper have been hung up to dry previous to the setting of the gelatine, the opposite corners to those by which the sheet was first suspended should be hung lowest. This secures a fairly even coating. The paper in this condition, even when damp, is slightly sensitive, and therefore it should be dried in a room which

only admits non-actinic light. It is exposed in the ordinary manner beneath a negative, which should be of a line engraving, and not in half-tint.[1] When the lines appear of a well-defined fawn colour on a yellow ground, the paper should be removed to the dark room for subsequent treatment.

If the object be to make a print to transfer to stone or zinc, the following ink should be prepared (though any lithographic ink will answer fairly well):

Lithographic printing ink . . .	16 parts by weight
Middle linseed varnish . . .	8 parts
Burgundy pitch	6 parts
Palm oil	1 part
White wax	1 part
Bitumen	2 parts

The ink and varnish are first mulled together with a muller, the Burgundy pitch and bitumen are next melted over a clear fire till all water is driven off, the wax next melted, and finally the palm oil. When properly melted they should readily catch fire, which shows that certain gases are being liberated. The ink and varnish are now well stirred into it, and the mixture run into the pots for storage. Should it be desired only to make a single print, the best ordinar chalk lithographic ink may be employed.

Where a lithographic press is available, a fine and even coating of one of these inks is usually given to a stone by means of a lithographic roller, the paper bearing the picture is then placed face downwards on it, and pulled through the press, by which plan a thin coating of ink is given to the entire sheet of paper. In the absence of a press the ink may be rendered liquid with turpentine, and an even film of ink may be given with a fine sponge.

To develop the picture the print is floated *back downwards* on a dish of water, having a temperature of about

[1] Partial success has been obtained by Sir Henry James in rendering even this latter class of work.

50°C., and is allowed to remain on it till the lines are seen as depressions. It is then removed on to a sloping board, and a stream of warm water, of about 70°C., is poured over the surface; the soluble gelatine, being in a hydrated condition, is carried away together with the ink that covered it, and the image is left, formed of ink resting on slightly raised ridges of insoluble gelatine. A very soft sponge dipped in the hot water and applied to the surface aids the development, in fact it can rarely be accomplished without it; but the most delicate touch is required for this part of the operation, as the ink on the fine lines is very liable to be carried away. The developed print is next washed in cold water, and then hung up to dry. In this state it is ready for transfer to stone or zinc, if transfer ink have been employed. It is beyond the scope of this book to describe the transferring operations: these are described in other works. A very convenient lithographic press, suitable for amateurs, has lately come under the notice of the writer; the figure on the opposite page will give some idea of its form.

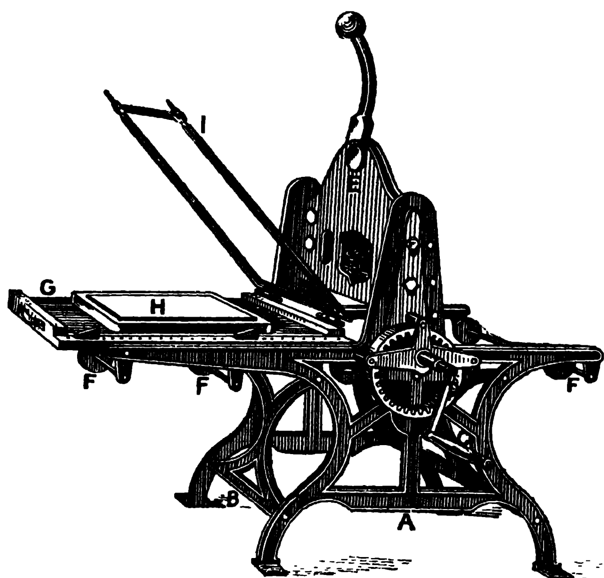
A A are the side frames, and B B are the stretchers or end frames, forming, when bolted together, the principal framework of the press. C is the handle, and D the pinion gearing into an inverted tooth-wheel by which the speed is diminished for economy of the power expended by the worker. E is the cross-head box, screw box, and scraper box. By regulating the screw the scraper is raised or lowered to suit the height of the stone H. The lever on top when depressed acts upon toggles contained within the box, which in turn exert a constant pressure upon the boxwood scraper, while the stone and sheet of paper are drawn underneath it by turning the handle C. When the proof is pulled the lever is raised and the stone returned to its original

[1] *Instruction in Photography*, published by Messrs. Sampson Low, Marston & Co.; or in Sir Henry James's work, published by Messrs. Longmans.

position free from pressure. G is the iron bed carrying the stone, and is carried to and fro upon the five friction rollers F.

Plates made of composition similar to solder are supplied by the manufacturer. They are excessively sensitive to

FIG.



greasy ink, and a number of impressions can be pulled off without clogging the work. To clean these plates all that is required is to wash out the old work with a solution of caustic potash, and then to scour the surface with fine emery powder. A dilute solution of acid is poured over the plate, and after washing under the tap, and gently warming, it is ready to receive a transfer.

Should only one copy of the picture be required, the

print, which should in that case have been printed in lithographic ink, is placed in a copying, lithographic, or typographic press, face up, and a slightly damped piece of white or other paper laid over it. When the pressure is brought to bear, the ink is retained by the latter, and a good impression is thus obtained. This method has been named by Sir H. James as the papyrograph. It must not be mistaken for another process, used for copying letters or circulars, and known by the same name.

Various modifications of this process have from time to time been proposed, such as coating the gelatine with albumen, but in the writer's experience, when a picture is to be obtained by *dissolving away* the gelatine, no better process than the above can be used.

Another process which differs from the foregoing is one brought out by the writer under the name of papyrotype. It is based on the fact that when light has acted on a gelatinised surface, then water is not absorbed. Thus by exposing a bichromated paper, prepared as in the above process, to the action of light behind a negative, the lines, which are represented by transparent glass in the negative, are printed through and the gelatine becomes non-absorbent, whereas the parts which have not been acted upon remain absorbent of water. If such an exposed paper be placed in water, and be then made surface dry, and a roller covered with a fine layer of greasy ink be passed over it, those parts which are non-absorbent will 'take' the greasy ink, whilst those which have taken up water will repel it. It does not need much intelligence to see that in this way a print in greasy ink is obtained which can be laid down to stone or zinc as desired.

Photo-lithography in Half-tone

It will be noticed that both these processes are best fitted for reproducing subjects which are represented by

lines, and it is a different matter to produce prints from the lithographic stone in half-tone. It is easy to reproduce on the printed bichromated gelatine a print of a half-tone subject in different blacknesses of greasy ink, but when such are laid down to stone or zinc the parts which should be half-tints become deep black, and the prints from the press become smudges of black interspersed here and there with patches of white. If the whole surface be grained we have a different result. Suppose for instance that embedded in the gelatine are very fine crystals which will dissolve in water, manifestly those parts which are most strongly acted upon by light will have the finest grain, the surrounding gelatine being unable to expand, whilst the parts which air has strongly acted upon will swell to a certain extent and leave a more pronounced grain in those parts.

Such is the artifice that Quartermaster-Sergeant Husband, R.E., has adopted in his process called papyrotint. With his gelatine and bichromate he mixes common salt and other such crystalline bodies, and coats paper with the mixture. When dry he exposes it beneath a half-tone negative and soaks it in water, and then passes a roller containing greasy ink over it. The lights and shades are in this way produced by greater or less fineness of grain, and as a result he is able to produce excellent photo-lithographs in half-tone.

There are several processes in the market to obtain the same result, but they are all more or less secrets; though it is believed that they all depend more or less on the grain given to the transfer which has to be laid down to stone.

CHAPTER XXIX

PHOTO-ENGRAVING AND RELIEF PROCESSES

NIÉPCE'S process, it will be recollected, was founded on the fact that a bitumen of Judæa, when exposed to light, became insoluble in its ordinary solvents if partially saturated. Silver plates were coated with bitumen, and after exposure the unaltered portions were dissolved away and iodine applied. The remaining bitumen was then removed, and the image was consequently formed of metallic silver on a ground of silver iodide. Had Niépce removed the iodide by any proper solvent he would have obtained a plate slightly engraved. Most of the present processes for photographically obtaining relief blocks, and also engraved plates, are based on the same principle as Niépce's ; in fact, there is very little departure from his mode of working until the biting-in commences. The student must distinguish between a relief and an engraved plate. The former is intended to be printed in the ordinary printing press, the portions representing the lines of the sketch being raised as in a woodcut, whilst with the latter they are in depression. An outline of a successful process for the production of either a relief block or an engraved plate in line will now be given.

A plate. is coated with a thin film of asphaltum or bitumen of Judæa, dissolved in chloroform or other convenient solvent, and after drying it is ready for exposure beneath a subject. If an engraved plate be required, the parts that have to be bitten in are the lines ; hence those portions must be protected from the action of light, since in order to lay the surface of the metal bare they should be covered with the soluble asphaltum. In taking a print from an engraved plate, the latter is reversed as regards left and right, therefore it is evident that a *reversed positive* should be employed, from which to print on the metal plate. For

the production of a relief block, by similar reasoning it will be found that an *ordinary* unreversed *negative* picture is required, as it is from its nature reversed as regards right and left. Whether a positive or a negative be employed, the opacity should be extreme on those portions which are to protect the sensitive layer from light. Such a positive or negative is placed in contact with the plate, and exposure given till it is judged that sufficient insolubility is given to the exposed portions. The soluble portions are then dissolved away by a solvent which is nearly saturated with the asphaltum. If the manipulations have succeeded, the metal should be perfectly bare in parts. Steel, copper, or zinc plates may be employed for this work; the two former are more especially suitable for engraving. The mordant usually employed for these may be a mixture of hydrochloric acid with potassium chlorate, which causes an evolution of chlorine. For zinc, hydrochloric acid alone may be employed, though it is well previously to dip the plate in a solution of copper sulphate. For an engraving the biting-in need be but very slight, though much, of course, must depend on the nature of the work as shown by the thickness of the lines. The thicker the lines the deeper must be the biting-in. For a relief block the biting-in has to be carried to a far greater extent; in fact, as deeply as seen in an ordinary woodcut. This involves very tedious manipulation after the first biting. The plate has to be warmed, dusted with resin; again heated to slightly melt the bitumen, so as to allow it to flow down the sides of the bitten-in lines. This process has to be repeated till a sufficient depth is attained. When there are larger spaces of white in the print, the metal is usually removed by a fine saw, or a graver. Relief-block making is essentially difficult in almost every stage, and rarely repays an amateur the labour he may bestow upon it.

Ehrard, of Paris, has another method of producing engravings, which is also dependent on biting-in. He pre-

pares a transfer, as for zincography, and, after going through the usual manipulations to transfer it to a copper plate, he plunges it into an electro-plating bath for a few minutes, thus covering the copper with a thin film of silver, the lines of the engraving being protected by the greasy ink. After a rinse in dilute acid the plate is transferred to a bath of mercuric chloride, where the silver is converted into the double chloride. After washing, the ink is removed, and the biting process allowed to proceed. The details of this process are a secret, but what is stated above gives a general idea of the process. The analogy that exists between this and Fox Talbot's process of engraving a daguerreotype plate is obvious.

Another process for obtaining the same results, various modifications of which have from time to time been announced, is due to Talbot. It consists of printing the negative on a gelatine film, washing away the unaltered gelatine, and making an electrotype from it. In the trade there are several firms who practise either photo-engraving or relief-block making, but it is not known which methods they adopt, as the several processes are kept secret. Amongst these may be named Goupil, Gillot, and Dujardin, of Paris; Dallas, and Leitch & Co., of London. Scamoni, of St. Petersburg, also makes very beautiful reproductions of engravings &c. His method seems to be based on the building up of a relief on the negative itself, and then taking an electrotype. Fig. 48 is a print from a half-tone block by the use of a cross-line screen as described at p. 251.

The processes above described are adapted to the reproduction of line work in contradistinction to half-tone drawings or photographs from nature. The production of photo-engraving or photo-etchings in half-tone is also much practised; and there are two methods by which they can be done. One is by first graining a plate with some grain, and then transferring to such a plate a gelatine cast in half-tone, and biting this with some etching chemical. Such a



ARCH OF SEVERUS ROME

process was that which Fox Talbot worked in the early days of photography. He gave a grain to a smooth copper plate by pouring on to it a solution in ether of camphor and resin. This gave a thin layer of resin and camphor, and a gentle heat expelled the latter and left the former on the plate in small granules. A stronger application of heat caused the resin to adhere to the copper surface. On such a plate he poured gelatine and bichromate of potash, and exposed it beneath a *positive* to the action of light. Where the light acted strongly it became more impervious to water, and where least, was quite pervious. When printed he placed the plate (waxed on the back) in a solution of ferric chloride; the solution bit into the copper surface almost proportionally to the intensity of the light that the different portions had received. The parts of the plate where the grain of resin rested remained more or less unacted upon: the deeper the biting, the more the grain was 'under-bitten.' Thus the grain was least in the deepest portions, which represent the deep shades of the picture, and greatest where the biting was least.

Several of Fox Talbot's plates produced in this manner gave the promise of the great things which have been effected by a slight modification of his process. It is believed that several processes in the market are really Fox Talbot's original one improved in detail; and this method of producing half-tone plates is by preparing a gelatine mould, the surface being grained, and taking an electrotype from it. It is believed that Goupil's process and others also are based on this principle.

We cannot quit this subject without remarking that some very beautiful half-tone typographical blocks were produced by Pretsch as early as 1858, his process being based on that of Talbot, already mentioned.

Half-tone Blocks

The illustrations of many periodicals of the present day are made direct from photographs, and a brief description as to how these are produced is given.

An ordinary magnifying glass will show that in the prints the dark shadows are produced by means of black dots of some size close together, while the highest lights show dots equally spaced as before, but considerably smaller in area. The half-tones show similar equally spaced dots, but intermediate in size. The negative from which these dots are produced must evidently show points of transparency all over, but of varying size. The dots are produced by placing near the plate to be exposed to the picture a glass containing a very fine network of opaque parallel lines ruled in two or even more directions. If such a network were placed in contact with the plate, it would evidently impress the picture during the exposure with a sharp transparent network of lines, and the interspaces would be filled with deposit more or less opaque according to the brightness of the image impressed upon it. When, however, the network of lines, generally ruled on a flat glass plate, is a little removed from the plate the dots become more opaque, but larger or smaller according to the brightness of light acting. The explanation of this—though it must be said that other explanations have been offered—is that each little square or space of transparency formed by the intersection of the lines acts as a pinhole, and that the image formed by each one is the image of the diaphragm of the lens illuminated by the light of the picture which would fall on that particular part of the plate. This indicates that the shape of the diaphragm has something to say to the filling in of the dots.

If we isolate one of the interstices of the ruled screen, and view a point of light through it, it must evidently act as a pinhole does. If the interstice be circular, and the

image of a monochromatic point of light be viewed, we shall find that when the screen is moved away from the focussing screen on which the picture is sharply focussed the image of a point of light is first a white dot surrounded by a black ring, and then a black dot surrounded by a white ring, and these alternations take place at different distances. When the central dot is black the image will appear smaller.

If we next use two pinholes close to the lens, and which occupy, say, extreme corners of where the aperture of the diaphragm to be used would come, two such pinhole images would be found side by side and overlap. If we make pinholes at the other corners we shall have two more images overlapping each other and also the first two; as the number of holes is increased we shall have more overlaps. If the diaphragm aperture be circular the central part of the image will be most intense, and the image itself will occupy a smaller area than the interstice. The larger the aperture of the diaphragm (of course within limits) the more will be the spreading of the image on the ground glass or the plate. These phenomena may be seen on photographs taken, or they can be seen well by using a focussing glass pressed against a plain glass which replaces the ground glass of the camera. The above experiments show that the shape of the aperture of the diaphragm must alter the shape of the dot impressed on the photographic plate. A square aperture, with its side placed at an angle of 45° with one set of the parallel lines forming the mesh is said to give the best results. The main point to arrive at is that in the high lights the opaque dots in the negative should coalesce in as many points as possible, leaving only a fine spot uncovered. There are certain regulation sizes of ruled screens found by practice as working well. The closeness of the lines desirable depends in a great measure on the coarseness of the paper on which the block is to be printed. With highly glazed paper the

ruling may be as close as 200 lines to the inch. In Penrose's 'Pocket Book,' it is laid down that

85	lines to the inch	for	a coarse block,
100	,,	,,	a moderately coarse block,
133	,,	,,	average work,
150 to 175	,,	,,	magazine work,

are suitable rulings. The width of the lines is important. It is found in practice that the thickness of the lines may be equal to the space they enclose, and should not be less than 4 : 5. The reason is evidently that if less the overlapping of the dots would be too marked.

The distance of the screen from the plate is manifestly important. Penrose says that if a small piece of thin microscopic glass be cemented on to the inside of the focussing screen (on which the image of the picture has been accurately focussed), and then the mesh plate be inserted parallel to it, a magnifier will enable the operator to judge of the proper distance to employ after the stop proposed to be used has been inserted.

The mesh plate should be moved to and from the focussing screen until the high light dots are joined corner to corner. The distance of the screen may vary between $\frac{1}{32}$ of an inch and $\frac{1}{2}$ an inch.

To obtain a negative in practice a reversing prism or else a mirror is used in front of the lens, and the picture, print, or drawing is illuminated with an intense light. (The best process to use is the wet-plate process, or the collodion emulsion process, as any degree of intensification can be given to the image when so produced.) The screen is inserted at the proper distance, the exposure made and the plate developed. Cyanide of potassium is used to clean the plate and to eat away any silver deposit alongside the dots, and the intensity is given by the cupric bromide intensifier or other similar one.

The following description of the preparation of the block is taken from 'Instruction in Photography:'[1]

Preparation of the Metal Plate.—The zinc or other metallic plate, having been cleaned with whiting and methylated spirit, may be coated with the bichromated albumen used for line work. Several other formulæ have come into vogue, among them the enamel process, for which a formula by Mr. W. Gamble is given:

Dried albumen	120 grains
Water	2 ounces
Mix thoroughly, and with it add ammonium bichromate	60 grains
Dissolved in water	2 ounces
And add ammonia (880°) . . .	1 dram
Add clarified Le Page's fish glue . .	4 ounces

And mix thoroughly with the albumen solution.

This formula is suitable for use with bright sparkling collodion negatives; for thin negatives and dry-plate negatives the quantity of fish-glue may be reduced. After mixing the froth should be allowed to subside and the solution then filtered. Preferably the solution should stand in a jar, covered with muslin to exclude dust, for a day before use. The plate is coated with the solution on a whirler. After printing, development is begun by soaking for a minute or two in cold water; the film is then tinted with a solution of methyl violet, 1 ounce, in water 20 ounces (filtered), and development is finished by rinsing in warm water (about 100° F.). When quite dry the plate is heated over a gas-stove till the film is burnt to a deep brown, almost to a black. To secure this colour the heat must be very intense—almost sufficient to melt the zinc plate.

Etching the Plate.—Etching is most safely conducted in a 1 per cent. solution of nitric acid, and may occupy from half to three-quarters of an hour. A stronger etching

[1] By Sir W. de W. Abney. (S. Low & Co.)

bath may be employed, but there is then a tendency for the film to lift. Success in etching depends to a great extent upon the quality of the negative. When copper or brass plates are used the etching fluid is a solution of ferric chloride registering 35° to 45° with the Baumé hydrometer. The operations of mounting &c. are as for the line plate.

Students who wish to acquire the working details as practised in commercial houses are referred to 'Half-tone on the American Basis,' by Wilhelm Cronenberg, and translated by William Gamble; and 'The Half-Tone Process,' by Julius Verfasser, both published by Percy Lund & Co., Limited; and are recommended to obtain lessons at one of the trade houses or at one of the institutions where the process is taught. Trade workers may obtain instructions at the Technical School, Bolt Court, Fleet Street.

CHAPTER XXX

PHOTO-COLLOTYPE PROCESSES

By a photo-collotype process is meant a 'surface printing' process, by which prints are obtained from the surface of a film of gelatine, or other kindred substance. The general methods by which such surfaces are formed are based upon the one fact already pointed out at p. 222, that gelatine, like other similar bodies, when impregnated with potassium dichromate, becomes incapable of absorbing moisture after full exposure to light; and that where light has partially acted, there it becomes only partially absorbent, when compared with the amount it will absorb when entirely guarded from light. Suppose we prepare a film of gelatine with which has been mixed some potassium dichromate, by

floating a warm solution of the mixture over a smooth surface, such as a thick glass plate, and when dry expose it beneath a negative in which we have different degrees of light and shadow, as in a landscape or a portrait negative; on immersing the film in cold water, we shall have a picture impressed in which the different degrees of shadow are represented by different degrees of relief. If the back of a similarly treated gelatine film be exposed to light previously to its immersion, the relief afterwards will be found to be much slighter. This is evidently a necessary consequence. If over either of these surfaces, when all superfluous moisture has been removed, a smooth soft roller carrying a fine layer of greasy ink be passed, it will be found that the greasy ink will adhere to the parts exposed to light in nearly exact proportion to the intensity of light which has acted on them.

With the film in which the relief is high the ink will take less readily, because the roller, even when tolerably soft, will fail to come in contact with the exposed parts. With the film having but small relief the difficulty will not be found. If such a film as the latter be now placed in a printing press, an impression from it may be obtained, but it will be found that as regards right and left the pictures will be reversed. A reversed negative is therefore necessary. Theoretically the number of impressions which can be pulled from the surface is not limited, if the surface be kept damp, and if a fresh application of ink be given by the roller. It will be found, however, that after each pull there is a tendency of the unexposed gelatine to adhere to the paper, and thus to spoil the printing surface. In order to prevent this it has become customary to introduce into the gelatine some substance which will harden it. Certain gum resins, alum, chrome alum, and kindred substances effect this hardening, and one or other of them is to be found in the formulæ given for most of these processes. Albert, of Munich, may be said to have first discovered a thoroughly

workable process, based on the above principles, and we shall briefly give an outline of the method he adopted as being a typical one, and unencumbered with any of the large number of modifications introduced at various times by other experimenters.

A piece of plate glass some two centimetres in thickness is coated with a gelatine mixture made as follows :

I

Good glue	10 grammes
Water	80 c.c.

II

Potassium dichromate . . .	3 grammes
Water	40 c.c.

These are dissolved separately and mixed warm. The plate is then coated and dried by heat, five or six hours' exposure to a temperature of about 60°C. being sufficient to effect desiccation. The plates are now exposed back uppermost to light for about a quarter of an hour, the gelatine films resting on a smooth black surface, after which they receive over the first a second coating made as follows :

Gelatine	8 grammes
Water	100 c.c.

II

Potassium dichromate . . .	3 grammes
Water	40 c.c.

To No. 1 is added 60 c.c. of white of egg, and after heating to 60°C., No. 2 is mixed with it, and the solution is filtered through cotton-wool. This coating is dried. and the plate is ready for printing. The exposure depends upon the quality of the light; it must be continued till the whole of the details are visible on the gelatine, and much of the success depends upon the depth to which it is

carried. When judged sufficiently printed, the back of the plate is again exposed to light to such a degree that the resulting relief when the film is wetted will be small. The film is now washed to remove all excess of the dichromate, and is again allowed to dry. The dried plate is next placed for five minutes face uppermost in a dish containing a 25 per cent. solution of glycerine in water. The back is then embedded on the bed of a lithographic press by means of plaster of Paris, and is lightly rubbed over with linseed oil, and again slightly damped with water. A soft roller, charged with greasy ink, is then passed over the surface, when it is found that a perfect print appears on the surface. The plate, the surface of which is in contact with a piece of paper, is now passed beneath the press, and an impression pulled. Such a press as that in fig. 47 may be employed.

Mr. Ernest Edwards introduced an important modification of the above by mixing chrome alum with the gelatine to harden the gelatine film. He only uses one coating to the glass plate, and when dried strips it from the glass surface, and prints it in this condition. He retransfers the film to a pewter or other metal plate, and pulls an impression from it when thus supported. By this device the danger of destroying the printing surface, owing to the possible breakage of the glass plate, is overcome, and in consequence the cost of production is diminished. For a full description of the process, which is named 'Heliotype' by the inventor, the student is referred to another work.[1]

It is scarcely possible to enumerate all the different collotype mechanical processes. We may mention in England, the autotype, Pumphrey's, the heliotype, and the phototint processes as being amongst the most successful.

[1] *Instruction in Photography.* Sampson Low & Co.

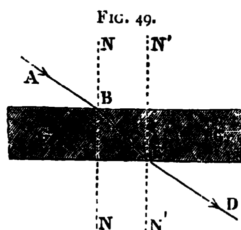
CHAPTER XXXI

ELEMENTARY PHOTOGRAPHIC OPTICS

WITHOUT entering into any discussion as to the theory of light, it will suffice to glance at the more general laws of geometrical optics, such being sufficient to show the principles on which photographic lenses have been designed.

A ray of light, whilst passing through a medium of uniform density, travels in straight lines, and when a ray of light passes from any medium to one more dense, at any angle less than a right angle to the tangent of the common surface, the direction of the ray of light is bent in towards the normal of the common surface; and if the rays pass from a medium to one less dense, it is bent away from the normal. Fig. 49 explains what is meant by the above. Let G G represent the section of a thick sheet of glass with parallel surfaces. Let a ray of light, A B, strike the top surface of the glass at B. Glass being a denser medium than air, the ray will be bent in towards the normal, N N, of the surface, and strike the lower surface of the glass at C; on the ray of light emerging from C to the air it will be again bent away from the normal N′ N′, and move in the direction C D, which is parallel to A B, since the surfaces of the glass plate are supposed to be parallel.

FIG. 49.

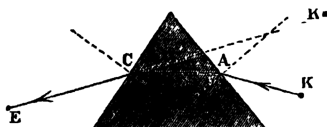


It is found experimentally that the sines of the angles which the ray makes with the normal at the surface of the two media have a fixed ratio to one another, and that this coefficient is dependent on the media through which the ray passes. Thus from air to ordinary flint-glass the coefficient is about 1·5, and from the flint glass to air the reciprocal about $\frac{1}{1\cdot5}$ or ·66. Applying plane trigo-

nometry to this experimental fact, it will be found that there is a limit to the angle at which a ray of light can pass from any medium to one less dense, since the limit of the sine of an angle is unity. When the ray strikes the surface at this particular angle or at a greater the rays are reflected back, and the limiting angle itself is called the critical angle, or angle of total reflection, for these two media. A reference to this is made in a subsequent chapter.

Instead of the surfaces of the glass being parallel we may have them inclined at an angle to one another, and in this case the refraction at each surface will follow the same law. An object which is really at K, fig. 50, will appa-

FIG. 50.

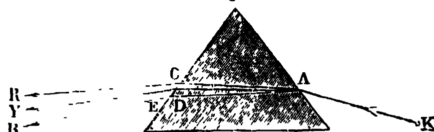


rently occupy the position K′, which is equivalent to saying that a ray of (monochromatic) light projected in the direction K A would have a direction C E after passing through the prism.. If the projected beam of light in the direction K A be white, it will be found, as already noted in the second chapter, that on emerging from C it is split up into rays of the different rainbow tints. If we take any three distinctive rays in the red, yellow, and blue, we shall find that the red is least refracted and falls in a direction R, fig. 51, the blue most and falls at B, and that the yellow occupies the intermediate position. This difference in the index or co-efficient of the refractive power of the media for different coloured rays gives the phenomenon known as dispersion.

It is found by experiment that the angles formed by

the directions of the different rays of light vary according to the composition of the glass employed for the prism; that with one specimen, for instance, the angle formed by R and Y does not bear the same ratio to the angle formed by Y and B that it does when another specimen is employed.

FIG. 51.



It is owing to this difference in dispersive power of various glasses, that it has been found possible to cause the component rays of white light to be nearly equally refracted, and yet to show no appreciable colour, due to dispersion. It will be seen in fig. 52 that, by employing opposing prisms of different composition, the dispersion may be almost entirely overcome. Thus it may happen that by placing a prism B of the dimensions, and in the position shown, the rays originally forming white light, and which were decomposed by the prism A, might be so bent, owing

FIG. 52

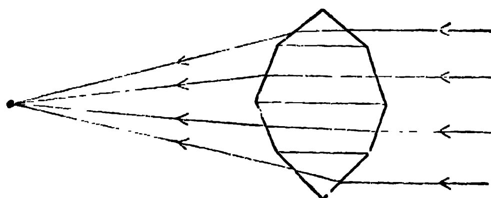


to the difference in the dispersive power of two media, that they emerge from B parallel to each other, instead of each ray forming a definite angle with its neighbour, and that still the original ray may be refracted. Supposing B and A to be of the same homogeneous medium, it is evident that

the same result would not be obtained. If the distance between B and A were diminished till the adjacent surfaces touched, the parallelism of the rays emerging from B would still be obtained, and, owing to the small dispersion of the rays in A, an incident ray of white light would emerge as white light. The two media we have been supposing to be employed are only hypothetical. Unfortunately up to the present date no two media have been found whose dispersive power can be utilised so as absolutely to correct one another.

Supposing we have a series of prisms and their frusta joined together as shown, it is evident that the surfaces may

FIG. 53.

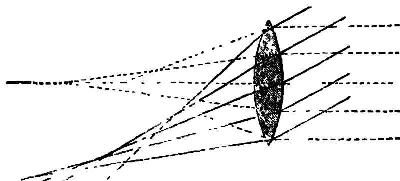


be worked at such angles that the rays of light proceeding from an object at any distance from them may cut in one point and form an image of that object. In the figure 53 we have supposed the luminous object to be infinitely distant and to form one single image. By rounding off the angles the same result may still be obtained and will form a lens. The curve that a glass would take, to give such theoretically perfect results, would be practically unsuitable, owing to the difficulty of grinding it; and also because it would only be correct for a particular distance and direction of object. In practice lenses are worked to spherical surfaces, as being most convenient, and being capable of approximate accuracy.

We will first glance at the inaccuracy that the spherical

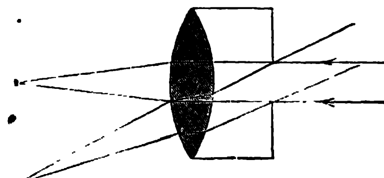
surface may cause when uncorrected by other means. If the rays of light, striking the lens obliquely, or along its axis, be reflected from any distant object, they will be practically parallel rays, and if different annuli of the lens be covered up, it will be found that the point of intersection of

FIG. 54.



the rays will vary, the intersection of the marginal rays will be nearer to the lens than that of the central rays, fig. 54; thus when the whole of the lens is utilised the object will appear wanting in definition owing to what is called 'spherical aberration.' This defect is overcome in a great measure by placing a diaphragm in front of the lens, fig. 55, the oblique rays and the central rays passing through which

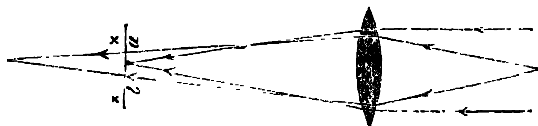
FIG. 55.



can be brought approximately in focus on a plane at right angles to the axis of the lens. Again, a diaphragm has a further advantage in that it allows the foci of a distant and a near object to lie on one plane. The nearer an object from which the rays proceed is to the lens, the longer will be

the focus after they pass through the lens. Let the rays issue from a distant and a near object. From fig. 56 it is apparent that if the whole lens be used (supposing spherical aberration eliminated) there would be no plane, x x, on which the two objects would appear at all defined. The effect of a diaphragm, or 'stop,' as it is technically called,

Fig. 56.



is to narrow both pencils of light so that neither of them is much out of focus at any point intermediate between the foci of the extreme rays. See fig. 57. This will be entered into further on in this chapter.

Supposing that the rays from the near object formed an angle with the axis of the lens, and those from the distant object coincided with it, a larger diaphragm might be

Fig. 57.

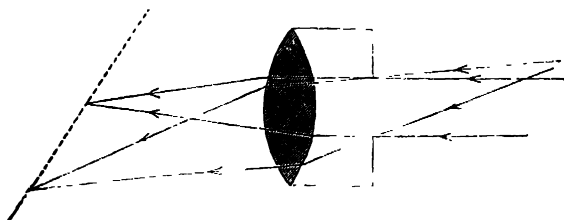


employed if the plane on which the images of the objects have to be received makes an angle with the axis of the lens, fig. 58. It will be seen that the swing-back of a camera serves this purpose.

It is to be observed that nearly the same results can be obtained by placing the diaphragm behind the lens instead

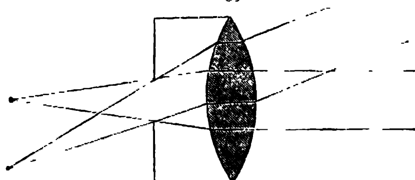
of in front, fig. 59; and also that the size of the diaphragm determines the brightness of the image, for only a portion of the lens is utilised.

Fig. 58.



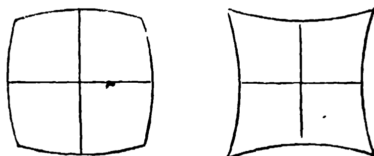
With a lens such as shown there is a difference in the resulting images when the diaphragm is placed in front or

Fig. 59.



behind the lens. In both cases we have distortion, but the distortion in one case is the reverse of that in the other.

Fig. 60.

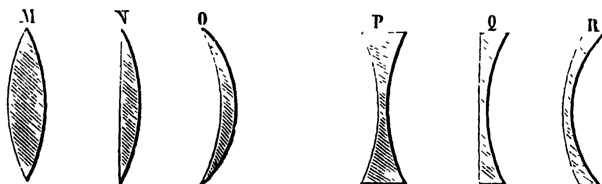


When the diaphragm is in front of the lens the image of a square would be barrel-shaped. When it is behind the curvature would be reversed, fig. 60. It would be useless in

either case to take an architectural subject with such a lens unless the building occupied but a small proportion of the picture. The reason of this distortion will be apparent when it is remembered that the margin of the lens, its surfaces being portions of spheres, will cause greater refraction than the central portion. When the diaphragm is in front of the lens it is the margin of the lens which gives the image of the corner of the square. The image of the centre of each side is formed by a portion of the lens which is more central, and therefore is less proportionally bent. When the diaphragm is behind the lens different portions of the lens are used to form the image, and consequently the distortion is reversed. By placing a lens on each side of the diaphragm it is evident that distortion due to this cause may be entirely overcome, and thus we get what is called a doublet lens. It will be found that with certain lenses, if we attempt to obtain a sharp focus of horizontal and vertical lines near the margin of the focussing screen, we shall fail; either the one or the other will be indistinct. This is due to *astigmatism*, a defect also caused by the spherical form given to the surfaces of lenses.

Lenses have various shapes given to them; the following are the different forms:—

FIG. 61.



M is the double convex; N, a plano-convex; O, a concavo-convex; P, a double concave; Q, a plano-concave; R, a meniscus. Lenses in which the concavity is greater than the convexity can have no actual but only a virtual focus, as may be seen by making a diagram. All such, when

combined with other lenses, in which the convexity preponderates,[1] will either increase the focal length or give a virtual focus to the combination. In photographic lenses the chief use of concave lenses is, by making them of suitable glass, to secure achromatism.

The principal focus of a lens is the point where rays which enter parallel meet on emergence. As an example we may refer to fig. 56.

The optical centre of a lens is that point in the axis of the lens through which lines joining any points in an object and their images would intersect.

Any point in any object and the image of that point are said to be the conjugate foci of the lens; and the conjugate focal distances are said to be the distances of the optical centre of the lens from these two points.

The equivalent focus of a lens is a term applied to a compound lens. It is the focus of parallel rays entering the lens. It is termed equivalent from being compared with a single lens that would produce the same sized image at the same distance from the object.

To find the practically focal length of a combination of lenses, measure a distance of say 50 metres away from some fixed point, and place a rod at the extremity. From this rod measure a line of say 10 metres in length, exactly at right angles to the first line, and place a rod over this point. Now place the front of the camera exactly over the starting-point of the first line and level it, the lens being in the direction of the first line. Having marked a central vertical line in the ground-glass with a pencil, focus the first rod accurately, so that it falls on the pencil line in the ground glass. Take a picture of the two rods in the ordinary manner, and measure back as accurately as practicable the distance of the centre of the ground-glass from the

[1] The material in which the lenses are worked must be taken into consideration in determining this.

starting-point, and also on the negative the distance apart, at their base, of the images of the two rods.

Suppose the first measured line—

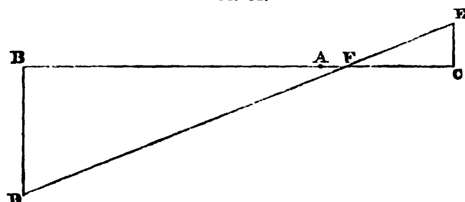
A B to be 50 metres; B D, the second line (the distance apart of the rods), to be 10 metres; A C to be 30 centimetres; and E C, the distance apart of the images of the bases of the two rods, to be 6 centimetres.

Then B D + C E : C B :: C E : C F, which is the equivalent focal distance :

$$\therefore \text{CF} = \frac{(50 + \cdot 3) \cdot 06}{10 \cdot 06} = 30 \text{ centimetres.}$$

It is, therefore, this distance along its axis from the ground-glass of the camera to the optical centre of the lens.

FIG. 62.



The student will readily devise the means of setting off the distance thus found on the brasswork.

It would be out of the scope of this work to touch on the higher mathematics of optics, and the following formulæ are only true when the thickness of a lens may be neglected.

The relation of the conjugate foci to one another is expressed by the following formula :

$$\frac{1}{v} = \frac{1}{f} - \frac{1}{u}.$$

Where v is the distance of the optical centre of the lens from the ground-glass, u is the distance of the optical centre of the lens from the object to be photographed, f is the

equivalent focal distance. From this it will be seen that if u is very great, then $\frac{1}{u}$ is so small that it may be neglected, and there remains $v=f$. That is, the image of an object at a great distance will be at the equivalent focal distance.

Applying the above formula, suppose we have a lens where $f=30$ centimetres and $u=40$ centimetres :

$$\frac{1}{v}=\frac{1}{30}-\frac{1}{40}=\frac{1}{120}.$$

That is $v=120$ centimetres, or the distance of the ground-glass from the centre of the lens must be 120 centimetres to bring it into focus.

Let it be required that u should be n times greater than v, which is the same as saying that the image must be $\frac{1}{n}$ the size of the object.

Then—

$$\frac{1}{f}=\frac{1}{v}+\frac{1}{nv}=\frac{n+1}{nv};$$

or

$$v=\frac{f(n+1)}{n}.$$

Suppose, as before, $f=30$ centimetres, and it is required to diminish the image of an object to $\frac{1}{4}$ of the size of the original :

$$v=\frac{30(4+1)}{4}=37\cdot5 \text{ centimetres},$$

$$u=nv=4\times37\cdot5=150 \text{ centimetres},$$

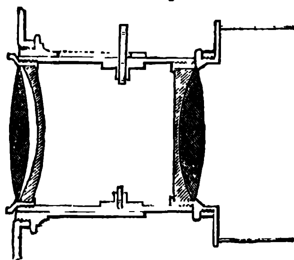
or the ground-glass must be 3·75 centimetres and the object 150 centimetres from the lens.

By similar reasoning, if the object is to be enlarged four times, it will be found that the above distances must be reversed.

In choosing a photographic lens the purpose for which it is required must be kept in view, for it will be evident that the requirements necessary may be different. In a

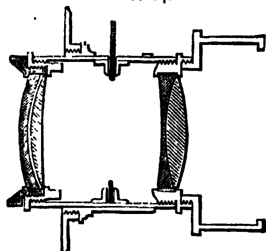
lens for taking portraits we have, for instance, certain properties which are not essential, and even might be detrimental in a lens for taking landscapes. With the former the objects to be photographed are generally within a few feet of it, and there are a variety of points situated in different planes which ought to be impressed with sharpness on the photographic plate, and that without any distortion. The last desideratum puts the employment of a single lens out of the question unless a small stop be used, and it is evident that a double lens must be used. Starting with this, it is quite evident that the curves of the surfaces of portrait lenses must vary from those for landscape work, and must be so designed as to be capable of delineating points in different planes not far from the lens itself. It will be found that this can be secured by combining lenses of the same or different focal lengths, separating the pairs by a long interval. This limits the extent of field and necessitates the employment of object glasses of wide diameter in order to cover a sufficient area. In practice the lenses are so far separated that the amount of surface of the photographic plate which can be utilised for some purposes scarcely exceeds the diameter of the lens itself. Again, rapidity is an essential quality of a good portrait lens, and the curves of the surfaces of the lenses and their separation must be so adapted that, without the use of any diaphragm, they shall give a fairly sharp image of a figure or part of a figure when placed at a reasonable distance. Spherical aberration is a positive advantage for some of these requisites. Fig. 63 gives an idea of the curves and also the amount of separation which is given to the lenses

FIG. 63.



of a Petzval portrait combination, on the pattern of which many of the modern ones are still constructed. The dark shaded portions show the crown glass, and the light shaded portions the flint glass lenses.

FIG. 64.



In one of the beautiful portrait lenses introduced by Dallmeyer we have a decided variation from this model. The advantage of this lens, fig. 64, is that two components of the back combination are capable of being slightly separated, giving a greater depth though a more diffused focus than ordinarily obtainable.

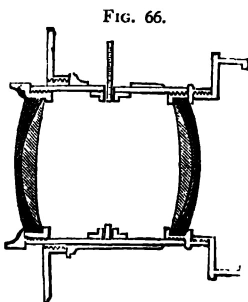
For landscape lenses it is not so necessary that points lying on different planes near the lens should be brought in focus on to the photographic plate, but that objects at a distance from the camera, though lying in far different planes, should be sharply defined, and also that objects lying at a considerable angle from the axis of the lens should be in good focus. This latter requisite does not exist to nearly so large an extent in a portrait combination; hence, evidently, the curvatures of the lenses must be different, as also the amount of separation between the two lenses, when a double combination is employed. For ordinary landscape work there is nothing to prevent the adoption of a single lens, since the distortion produced by it would pass unnoticed, though, as already pointed out, architectural subjects demand freedom from all distortion, and, therefore, a combination of lenses has to be resorted to. All single lenses, for certain optical reasons, have the meniscus form given to them, and fig. 65 gives an idea of the forms adopted by some of the best makers.

FIG 65.



As already pointed out, the lenses are rendered achromatic, the achromatism being adapted for the actinic rays more than for the visual rays. Fig. 65, No. 1 shows a meniscus flint lens cemented to two crown concavo-convex lenses. No. 2 has a crown double convex cemented to a double concave flint lens, whilst No. 3 shows a crown concavo-convex lens cemented to a meniscus flint lens.

FIG. 66.



Of a combination of lenses for architectural work we show three examples. The first is of the 'rapid rectilinear' type, as made by Dallmeyer, fig. 66. It is formed by a symmetrical pair of lenses of flint and crown; the concave surfaces of the lenses face each other. If we call the focal lengths of the combination 10·5 in., the focal lengths of each lens will be found to be about 20, and the separation between the two lenses to be about 2 inches.

It may be useful to give a rule for ascertaining approximately the focal length of any pair of lenses when combined.

Multiply the focal length of one lens by that of the other, and divide by the sum of their focal lengths less the distance of separation. In the above case we have—

$$f = \frac{20 \times 20}{40 - 2} = \frac{400}{38} = 10{\cdot}526.$$

The diaphragms for this combination occupy a position half-way between the symmetrical lenses, and therefore give no distortion. This lens covers an angle of about 60°.

The next lens, fig. 67, is what is known as a 'wide angle' doublet, in which the separation between the lenses is very small, and their foci considerably shorter, in proportion to the area of the circle that it is to cover. Some of these com-

binations are made so as to cover a circle whose diameter subtends an angle of 90° from the optical centre. The objection to these lenses is the unequal illumination and the small stop that is obliged to be employed with them, and their consequent slowness.

Fig. 67.

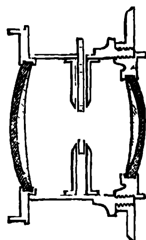


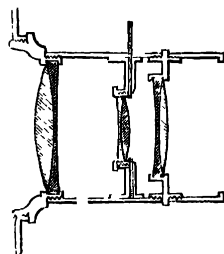
Fig. 68 shows a section of the 'triplet lens,' in which the place ordinarily occupied by the diaphragm is replaced by a third compound meniscus lens. There were certain advantages connected with this lens at the time when it was introduced, but since the manufacture of non-distorting doublets giving a fairly flat field has been perfected they are comparatively obsolete. It is, however, a good illustration of the ingenuity with which opticians aimed to meet the requirements of photographers.

In the doublet lens the position of the diaphragm is important, otherwise—as can well be understood—the second lens will not correct the distortion of the first. In the case of a doublet in which both lenses are symmetrical, the diaphragm should naturally occupy a position half-way between them. If the focal length of the front lens be different from that of the back, the diaphragm must occupy a position proportional to the focal length of the lenses.

With certain classes of doublet lenses as formerly constructed there was formed a fogged central patch on the exposed plate. This was due to what is called a 'flare spot,' which is a circular patch of light seen on the ground-glass immediately in a line with the axis of the lens. It is really an image of the opening in the diaphragm. If glass were perfectly transparent, such a defect could not exist; but, owing to its reflecting light from its surfaces, it has a reality which is often very troublesome. The surface of the lens reflects the aperture in the diaphragm and forms a

distinct image of it, and if this image happen to coincide with the focal distance of the lens, the flare spot is sure to make its appearance. By slightly altering the position of the stop this defect is overcome. But, as will have been noticed before, the position of the diaphragm in a doublet lens is of importance for eliminating distortion; hence by curing this defect distortion might be introduced. By previously altering the distance of the separation of the two lenses, both evils may be avoided. At the best it seems, however, that the flare spot is really only distributed over the entire area which the lens covers. This reflection from the surface seems to account in a measure for the veil on negatives, which is often apparent when using certain slow lenses where bright objects have been photographed, and the exposure prolonged to enable the details in dark shadow to be capable of development. The veil is probably the photograph of the illuminated lens.

Fig. 68.



We must again revert to the diaphragm, or 'stop,' in order to give some further idea of its use, and also of the necessity which may exist for using one of large or small aperture. In the case of a single lens we have already shown that the position of a stop affects the shape of the distortion, which depends upon its being placed in front or rear of the lens. It may now be stated—and the reason will be apparent on examining the previous figures—that on the *distance* of the diaphragm from the lens is dependent the *amount of distortion*, as is also the size of the picture which the lens is capable of defining; whilst at the same time the flatness of the field is also in a great measure due to a large distance being maintained between them. In constructing a lens, then, an optician has to hit a mean in

order to give a satisfactory result. From these remarks it will be evident that a lens which embraces a wide angle should give least distortion, because the diaphragm must be necessarily closer to the lens than when the angle is curtailed. It is for this reason that the employment of a wide angle lens, with a plate of a size larger than that it was constructed to cover, is found to yield more satisfactory pictures than if a lens capable of embracing a less angle be employed. Thus a wide angle landscape lens intended to be used for a 40 × 30 centimetre plate, gives more accurate pictures on a 20 × 16 centimetre plate than does a lens embracing a more moderate angle when used for the same sized plate.

When a diaphragm is used, with the ordinary landscape lens or a double combination of lenses, there is a certain inequality of illumination of the field. The aperture of the diaphragm is for obvious reasons circular, and when the rays of light strike this in any direction but axially, it is evident that the admitted light must be diminished, varying in fact as the cosine of the angle the rays make with the axis of the lens. Thus the margins of the picture will on this account have less illumination than the centre. Another cause of the falling off of illumination is this:—If we have two equally bright and equidistant objects, so placed that the image of one falls on the margin of the plate and of the other at the centre, the area occupied by the first image will be greater than that occupied by the second, and consequently the marginal illumination will be less. Mr. Dallmeyer states in the first of two articles[1] which he has written on this subject, that 'the diminution of light from the centre towards the margins of the pictures from both these causes increases rapidly with any increase of *angle of view* beyond 40°. At this obliquity the extreme margins only receive 80 per cent. of the light falling upon the centre, at 50° it is reduced to 70 per cent., at 60° to 55 per cent., at 70° to 45

[1] *Year Book of Photography*, 1876 and 1877.

per cent., or less than one half. Therefore the larger the angle included in the picture the more apparent becomes the defect.' In the same article Mr. Dallmeyer insists that the aperture of a diaphragm should always be expressed in terms of the focal length. Thus an aperture of 5 centimetres when used with a lens of 50 centimetre focus, should be called $\frac{1}{10}$ aperture, which is a means of expressing the intensity of a lens. The aperture of the diaphragm also determines the amount of depth of focus, and this increases as the diameter of the aperture diminishes. Any point which is out of focus is represented by a disc of confusion, and when such a disc does not exceed a certain diameter, the eye is unable to distinguish it from a point. In practice 1 minute of arc is taken as the limit. When the diameter of this disc, as viewed from an ordinary distance for examining a picture (40 to 50 centimetres), subtends more than a minute of arc, the object will appear to be out of focus, whilst if less it will be in focus. Hence we may argue that the smaller the aperture of the diaphragm the greater the depth of focus there will be, since the foci of nearer objects and distant ones may all be made to fall within this limiting angle by diminishing it. A reference to fig. 57 will aid the student in comprehending this. Taking a disc of ·25 millimetre diameter, which is about a minute of arc as seen from a distance of 50 centimetres, as the greatest admissible diameter of disc of confusion, a table is readily constructed of the nearest point which will be in focus when any aperture of diaphragm is employed. Suppose we know the equivalent focus of the lens in question to be 25 centimetre focus, and that we are to use an aperture of 2·5 centimetres :

Taking the formula which will give an approximately true value—

$$\frac{1}{v} = \frac{1}{f} - \frac{1}{u},$$

when the distance is in focus, the nearest part of the foreground which can be considered sharp will have a focus

which is longer than the equivalent focus by ·25 centimetre, for

Cent. Cent. Millimetre.

$$2{\cdot}5 : 25 :: {\cdot}025 : x$$

$$x = {\cdot}25 \text{ centimetre};$$

$$\therefore \frac{1}{v} = \frac{1}{25} - \frac{1}{25 + {\cdot}25} = \frac{{\cdot}25}{25 \times 25{\cdot}25}$$

$$= \frac{1}{2525}$$

$$\therefore v = 25{\cdot}25 \text{ metres}$$

That is to say, all parts of the picture lying beyond 25 metres will appear to the eye to be in focus. The following table has been constructed on that basis: –

Intensity, or Aperture Ratio	Relative Exposures	Focal Length of Lenses in Centimetres: 10	15	20	25	30	40	50
		Distance of nearest distinct Objects in Metres						
$\frac{1}{10}$	1	4·1	9·1	16·2	25·2	36·3	64·4	100·5
$\frac{1}{15}$	2·25	2·7	6·1	10·8	16·9	24·3	43·1	67·2
$\frac{1}{20}$	4	2·1	4·6	8·2	12·7	18·3	32·4	50·5
$\frac{1}{30}$	9	1·4	3·1	5·5	8·6	12·3	21·7	33·8
$\frac{1}{40}$	16	1·1	2·4	4·2	6·5	9·3	16·4	25·5

The annexed formula will approximately give the nearest point p which will appear in focus when the distance is accurately focussed, supposing the admissible disc of confusion to be ·025 centimetre.

$$p = {\cdot}41 \times f^2 \times a,$$

when f = the focal length of the lens in centimetres,

a = the ratio of the aperture to the focal length.

The result is in metres.

It may be pointed out that excellent photographs, and which some people consider to be more artistic than those taken in the ordinary way, may be secured by the use of a pin-hole, in substitution for the lens. The size of the pin-

hole determines the sharpness of the picture. The writer has taken pictures, for comparison, with holes varying in aperture from a diameter of ·003 inch upwards. It may at first sight appear that the smaller the pin-hole the sharper the picture should be, but owing to the serious diffraction that takes place such is not the case. There is, in fact, one aperture which is best adapted for a particular length of focus, if we can designate the distance of the plate from the pin-hole by such a term. This the writer has calculated, and he finds that the aperture best adapted for any focus is expressed by the formula $d = 1{\cdot}25\sqrt{f}$, where f is the distance of the plate from the hole in metres and d is the diameter of the hole in millimetres. Thus, if the focal distance were one metre, the diameter of the hole should be 1·25 millimetre; if it were one-quarter metre, the diameter would be diminished to ·625 millimetre. It may be remarked that the puncture made by a common pin is suitable for a focal length of about one-fifth metre.

It must be recollected that a pin-hole picture is almost exactly of the same sharpness throughout, any difference there may be being due to the fact that at the margins of the plate the light penetrates through the aperture at a different angle, making it practically smaller; but if it be chosen of the most efficient size, as just described, the difference in sharpness will not be perceptible. There must be, as with lenses, a difference in the exposure given to the centre and the margins of the plate, owing to this same cause, and also to the fact that the surface of the plate is not at right angles to the incident rays. In calculating the exposure with a pin-hole the same rule must be applied as in calculating it for lenses with different apertures in the diaphragms, though, owing to the absence of all intervening glass, the pin-hole may have an advantage.

The student should remark that in doublet lenses the apertures in the diaphragms do not show accurately the available aperture of the lens. In order to ascertain their

correct value, a distant object should be focussed in the camera, in order that the focussing screen may be at the equivalent focus of the lens ; this screen is then removed and replaced by a glass over which is pasted any opaque paper. A candle is brought near the centre of the opaque screen in which a small hole has been punctured. The front combination of the lens is illuminated by the rays of light coming through the orifice, and the diameter of the disc of light seen on the front of the lens gives the available aperture of the lens when used with that diaphragm.

Since the introduction of Jena glass many new forms of lenses have been designed which permit the use of an aperture of $f/5{\cdot}6$ or $f/8$ to be used without loss of definition, and it is one of these we recommend to the notice of photographers. An historical account of photographic lenses compiled by Mr. R. Child Bayley will be found in *Instructions in Photography*,[1] by the author.

CHAPTER XXXII

APPARATUS

It will be unnecessary to describe much of the apparatus that is in daily use by the photographer, as some have already been described in various chapters, and some must be left to individual taste. In those kinds of apparatus which are to be described it must be borne in mind that the recommendations made are merely the results of the writer's individual experience, and it is not improbable that something better may be known to others.

Cameras.—It should be considered an essential in every camera, excepting one used for copying and enlarging, that it should have a back that at least will swing at an angle

[1] Sampson Low, Marston & Co.

away from the vertical plane, and it is a great comfort when a movement in a horizontal plane can also be given to it. Technically, the backs which can move thus are termed 'swing-backs.' The accompanying figure will give an idea of a double swing-back, and also of the kind of camera which for landscape work seems everything to be desired. A (fig. 69) is the front of the camera into which screws the lens L. The lens can be caused to occupy a position out of the centre of the camera by the double movement shown in fig. 70. *a* is the board to which the lens is attached by means of its flange sliding in the grooves *b b*, which are fixed on to the main movable front *c c*. This front also slides in grooves *d d*, attached to the body of the camera. These fronts are fixed at any point required by means of the screws *e* and *f*, which run in the slots as shown. Reverting to fig. 69 it will be seen that the camera has what is known as the 'bellows' form, the bellows B being attached to A and also to the swinging framework D. E is connected with R by means of a rod, passing through the side of the framework, and terminated by a clamping screw K. R can be made to approach or recede from A by means of a slow-motion screw turned by the handle X. D is connected with M by pivots which work in the brass plates H, and since C is fixed as regards the vertical plane, it is evident that D can move through any small angle about H, without in any way interfering with the other movements of the camera, and the angle can

FIG. 69

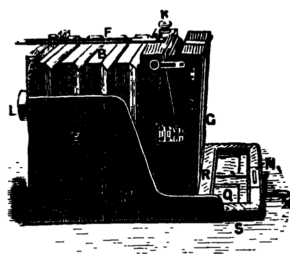
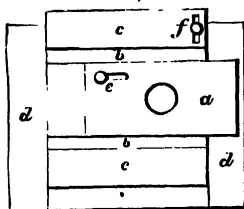
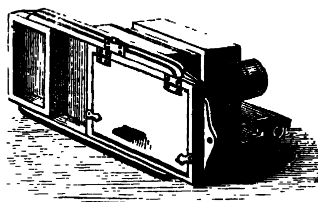


FIG. 70.



be maintained by clamping the screw, which works in a slot as shown. Thus, then, a swing away from the vertical plane is secured. The motion of D in a horizontal plane is secured by pivoting the frame M on to R. If the clamping screw K be loosened, M, and therefore D, can be moved through any small angle in a horizontal plane, and can be fixed in that position by tightening K. The double swing motions are therefore secured. F is a bar with a long slot cut in it, so arranged that clamping screws in C and A can fix it and give additional rigidity to the camera. When R has been moved along the tail-board Q, so that C touches A where the clamping screws M and K are loosened, the latter is free to turn up against the ground glass G. When a small pin

FIG. 71.



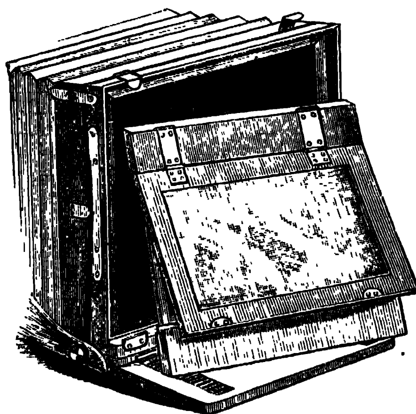
at S is withdrawn from P, this board, being hinged as shown, folds round the turned-up tail-board and Q is kept in position by means of a small snap spring fixed to the bottom of the camera.

The camera itself can be attached to the stand by the tail-board Q, in which position the greatest length of the picture is horizontal, or by E when the height of the picture has to be longer than its breadth. A camera 21 × 16 centimetres of this form, when packed in a leather case, weighs about 6 kilogrammes, or 14 lbs. For work in the studio where the diminution of weight is no object, a rigid form of camera can be adopted. Such a form we give in fig. 71. This is a camera adapted for taking cartes de visite, and it will be noticed that the alteration in focus is secured by a different

arrangement from that in the last. The front part, which carries the lens, slides outside the back part, the movement being effected by a pair of racks fastened on the base board, on which a long pinion works. Some photographers prefer this motion to that given by the screw, since the hands do not interfere with the position of the body whilst viewing the image on the screen.

It will also be noticed that there is a long carrier for the dark slides, and that the dark slide is more than double the length necessary to secure one picture. The object of this

Fig. 72.



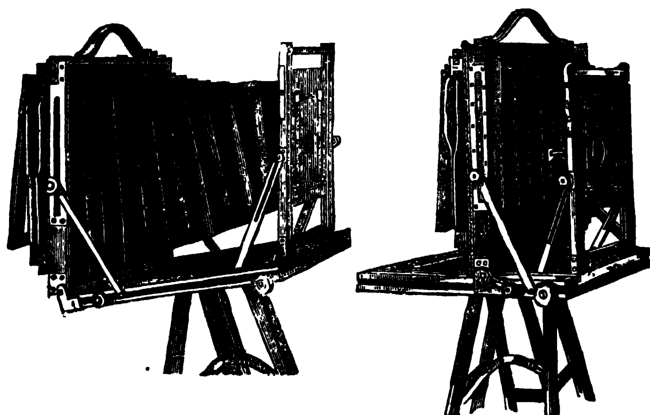
is to be able to give two exposures on the same plate, and thus to economise time.

It is very convenient to have attached to the camera what is known as a 'reversing back.' For this adjunct it is necessary that the camera should be square in section. Fig. 72 gives an idea of it. It will be seen that the slides fit into the back, which can be placed with the ground glass and plate having their greatest length horizontal or vertical. By this plan the camera can be utilised for taking pictures of either shape without any alteration except of the back itself.

The tendency of late years has been to lighten the camera for field use ; as an example of a type in which this is accomplished we may mention Watson's 'Acme' camera, which is compact when folded up and rigid when on the tripod (see fig. 73). The bellows is pyramidal, and it has a reversing back as above, and a rising and falling front which can also be swung to bring the lens central to the plate, and can be used with a very short focus lens.

One of the latest developments in photography is the use of the hand camera, which, as the name denotes, is a

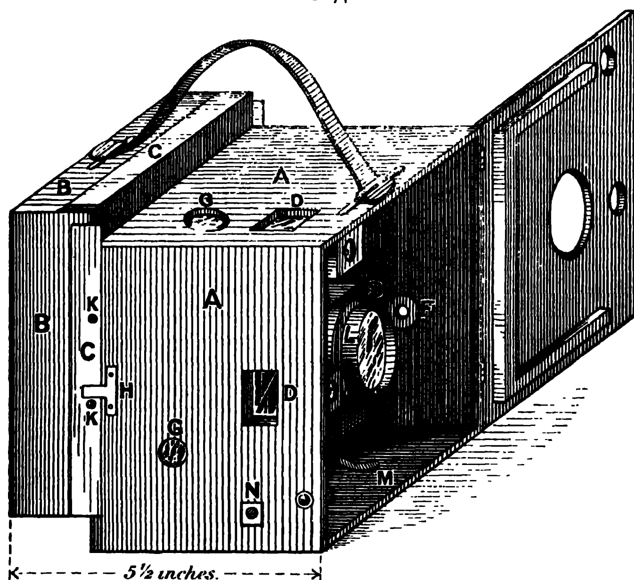
FIG. 73.



camera which is held in the hand. Mr. T. Bolas, several years ago, introduced what he called the detective camera, and it is believed that from this parentage the various forms of existing hand camera have sprung. Exposures given in these cameras when held in the hand must of necessity be of short duration, and it is rarely that an exposure of more than $\frac{1}{4}$ of a second can be given with any certainty that the resulting picture will not give evidence of a movement. For this reason, the exposure shutters supplied with them need not be timed to give a longer

exposure than this, nor to a shorter than $\frac{1}{100}$ of a second, owing to the speed to which, practically, the plate is limited. There are two types of hand camera: one in which there is a magazine of plates from which an unex-

FIG. 74.

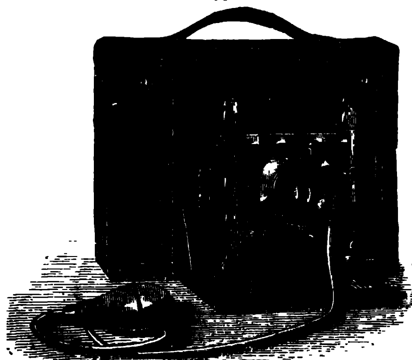


A A. The body of the camera, carrying a lens, L, and fitted with a roller-blind shutter, S, which acts behind the lens; this enables a change of lens to be easily made: the focussing is effected by screwing the lens in or out of a screw-socket attached to the shutter front. B B is a rising back for both upright and horizontal pictures; C C are brasses to guide the motions of the back, and H is a stop to check the back from going too far; D D are brilliant finders, and G G are levels. F is the bush for the tripod screw; M is the lever to set the shutter for time or instantaneous exposures; N is the exposure button. The camera is constructed to take plates in American pattern slides with draw-out shutters; it also takes a cartridge-roll holder as supplied by the Kodak Company (referred to page 285).

posed plate can be almost automatically supplied, and the other with which light-tight dark slides are used. The magazine camera is open to the objection that the plates are apt to collect dust on their surfaces, giving rise to minute

pin-holes in the negative on development, but the disadvantage of carrying loose slides is evident. Balancing the advantages of the two kinds, the writer gives the preference to slide-carrying cameras. A hand camera, of whatever form, should be strong, light, and free from any complication of movement which can get out of order; indeed, simplicity should be the main object. It should, if possible, have a rising front, for the purpose indicated with ordinary cameras, and should possess a mechanism to secure an adjustable focus. Some persons like to have a view-finder attached, but it is not necessary when the photographer has

FIG. 75.



had a little practice, and the writer thinks that a circular level is preferable, as it enables the camera to be kept horizontal. Fig. 74 gives an idea of a ¼-plate hand camera devised by the author.

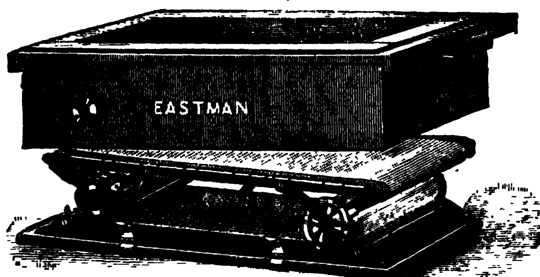
Cameras to carry rollable films only are practically the monopoly of the Kodak Company, who have various types, all excellent in design. In the larger class of kodaks—as, for instance, in No. 4 cartridge kodak—there is a means for raising the front for vertical as well as for horizontal pictures (fig. 75).

Cartridges of rollable film are now made which can be

inserted and removed by daylight, which is a great advantage.

The ideal camera is one which will take either plates or films. If the camera is constructed to take double backs with plates, the films can be utilised if the camera be fitted with one of these extremely useful 'cartridge-roll holders' which the Kodak Company supply (fig. 76).

Fig. 76.



For the outdoor part of dry-plate work the apparatus is comparatively small, and consists of a camera, focussing cloth, camera-stand, a set of double-back slides, or a single back adapted to a changing box, or some form of Warnerke roller slide if sensitive paper be employed.

A double back is of very simple construction. The slide is divided into two parts, hinged so as to fold one against the other, one portion carrying a thin blackened and hinged iron or tin plate. A sensitive plate is put in each half of the slide, the sensitised surface being outwards. The blackened plate prevents the passage of light from one to the other. The plates are placed in the camera as usual, and opened for exposure as with the ordinary slide.

It will be seen that for every couple of plates one double back is required, and it will seldom be convenient to carry more than three of these, on account of their weight.

It may be mentioned that a capital substitute for ground

glass may be made by coating an ordinary plate with the following varnish :

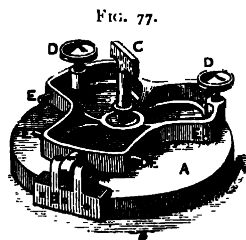
Ether	500 c.c.
Mastic	30 grammes
Sandarac	30 grammes

After dissolving these resins, benzine is added little by little till the grain becomes sufficiently pronounced.

In order to ascertain if the face of the sensitive plate in the dark slide occupies the same position as the ground-glass surface of the focussing screen, a bright object should be focussed accurately on the latter. The slide should next be filled with a piece of ground glass as if it were a plate, or a plate may be used. If the image retains the same definition it may be presumed the focussing screen is correctly placed. In wet-plate photography it is well to test the purity of the silver wires which are in the dark slide.

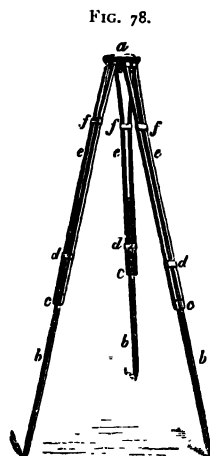
Camera-stands.—The camera-stand next requires a few remarks, as the comfort of working depends much on the form adopted. The essentials of a stand for landscape work consist of rigidity, lightness, and compactness when folded up. The annexed diagram gives a form which is convenient, though perhaps rather heavier than is desirable. It is on Kennett's principle, with a modification introduced by Lane. The inverted top is shown in the diagram, fig. 77. A is a circular mahogany disc to which is attached a brass hinge B of the form shown. On this hinge works the whole of the brass framework to which the legs are attached. C is a screw which passes through the centre of the framework, and also through the wooden disc, and it is by this screw that it is attached to the camera. It will be noticed that C has a collar half-way down, and that this

FIG. 77.



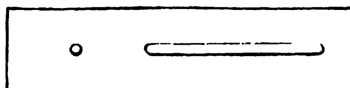
can clamp the camera to the disc when required. D D are levelling screws, by which the disc (and consequently the camera) can be accurately levelled. E E are pins into which the tops of the tripod legs fit. Fig. 78 gives an idea of the appearance of the tripod when ready to receive the camera. *c c* are brass collars which are fixed to the top half of the tripod. *d* and *f* are movable collars which respectively clamp the bottom half *b* of the top to the top half *e*, and the top half to the head to which the camera is attached. When not in use the head is detached, the bottom halves of the legs slide into the top halves; and they are strapped one against another and form a comparatively compact bundle.

Fig. 78.



The subject of the camera-stand cannot be passed over without mentioning the very ingenious method that has been made by M. Warnerke for combining ordinary pictures, taken from the same point, to form a panoramic view. In order to secure an accurate junction of two pictures taken from the same point, but in different directions, it is necessary that the lens and camera should revolve about the optical centre of the lens, for reasons which involve a study of the laws of perspective. By adopting the accompanying device, fig. 79, this can be secured. The camera-stand is screwed to the small hole, and the camera itself is

Fig. 79.



attached by a screw to some point in the slot. When the hole is vertically beneath the optical centre of the lens, and the camera is turned, it moves round the optical centre of the lens.

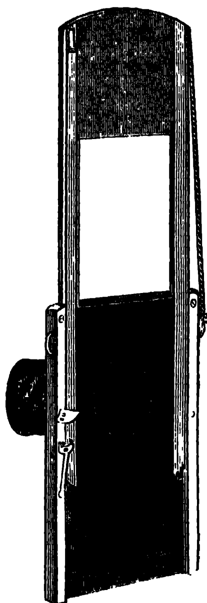
Lenses.—As regards the choice of lenses, it is very difficult to give advice. If the student is confined to the choice of one lens for landscape-work, he should unhesitatingly procure a doublet-lens, which has no perceptible flare-spot, and which embraces an angle of about 50°, since with it he can take both landscapes and architectural subjects. If he can afford another lens, perhaps a landscape wide-angle lens is next to be recommended, being exceedingly useful in a majority of positions and giving great brilliancy of picture. The most complete battery of lenses would be a rectilinear doublet, embracing an ordinary angle; a wide-angle doublet, to embrace about 80°; a couple of single landscape lenses, one embracing about 50° and the other about 70°.

For portraiture, the most useful lens is one which will give a 'cabinet' sized picture, and it may be supplemented by one of those quick-acting lenses, which are familiar to all portraitists of the day, for taking instantaneous pictures of children &c. It should be noted that many fine portraits and groups have been taken with the ordinary landscape doublet-lens, which, though slower than the portrait-lens, yet is sufficiently rapid to be usable.

Instantaneous Shutters.—In connection with lenses it is necessary that a word be said regarding the means of giving rapid exposures. In the market there are many numerous so-called instantaneous shutters which can give exposures from the $\frac{1}{100}$ second upwards. It may be well to slightly touch upon the rules which should regulate a properly made shutter. If the shutter be attached to the lens, first and foremost every action should be a double action, that is, if one part of the instrument moves up, another part should move down. The reason for this is that the centre of gravity of the whole apparatus (including in this the camera, the shutter, and

the legs) should remain as nearly as possible unchanged in position before, during, and after exposure. When the centre of gravity shifts, there is of necessity a vibration set up in the camera, with the result that the picture will not be sharply defined. Again, except in the final closing of the shutter, no part should be arrested with a jerk, for that will entail vibration. Thus, supposing we have a pair of shutters opening from the centre, the passage to and from the positions at which they will commence to close again should be as gentle as possible. Another point is that the whole aperture of the lens should be opened as rapidly as possible, and the principal part of the exposure take place when the whole lens is engaged in doing its work. The effective exposure may be taken as the sum of the apertures into the time during which such aperture is utilised. It will be evident, then, that the longer the full aperture is employed the greater will be the effective exposure in a given time. Hence two shutters may be employed which open and close the aperture of the lens in equal times, and yet one may give half as much more exposure to the plate than the other. The cheapest shutter is that known as the drop-shutter, and the maxims above laid down can be brought into play with it. The principle of a drop-shutter is the passing of an elongated aperture cut in a board over the front of the lens. The longer the aperture in the board proportionately to the aperture of the lens, the longer the latter is uncovered. If gravity alone be used as the moving power for the shutter, no great rapidity of exposure can be

Fig. 80.



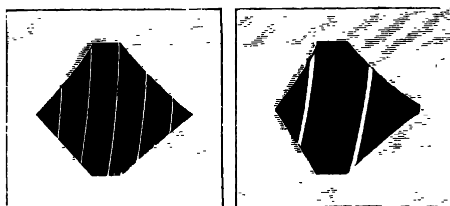
given to the plate ; but gravity may be aided by an elastic spring of varying tension, and so the times of exposure may be altered. A shutter of this description should not be attached to the lens, as there is only one part which moves, no counterbalancing movement taking place In practice it is well to attach the shutter by a velvet bag to the lens, and hold the shutter during exposure. The Thornton-Pickard Company have devised a series of roller-blind shutters suitable for either hand or stand cameras ; with these instruments both time and instantaneous exposures may be given, the length of the exposure being regulated by a milled disc with considerable nicety. The shutters may be attached either in front of or behind the lens, and the mechanism is so well balanced that no vibration is set up during the exposure. For very brief exposures upon moving objects the same company make a focal plane shutter in which the roller-blind, having a narrow slot in it, passes across and immediately in front of the plate.

The rapidity with which the shutter acts is a point which requires careful attention, as also is the question of its total efficiency. Both of these matters have recently been investigated by the writer, and the following is a *résumé* of the original paper published in 1892, in the Journal of the Camera Club. Perfect efficiency in a shutter may be said to be when during the whole time of exposure the entire aperture of the lens is uncovered, and when the whole of the plate is exposed at the same time, and for the same length of time. This is, of course, an ideal, and it would be most nearly reached were a pin-hole to be used, and the shutter placed close to it. The only shutter which gives an exposure to the whole plate at the same instant is one which works close to the diaphragm of the lens. In any other position one part of the plate receives exposure before another, and it depends on the equality of motion in the shutter whether each part receives the same amount of exposure. If a diagram of the movement of

a shutter, somewhat on the same lines as the diagram of a steam indicator, can be obtained, it is easy to ascertain what will be the effective exposure when it is placed in any position in regard to the lens, and when any diaphragm is employed. The method adopted was to place a slit at right angles to the line of motion of the shutter, and in the position of the diaphragm, and cause a beam of light to pass through it. This beam was received on a lens, and formed a horizontal image of the slit on a horizontal drum covered with sensitive bromide paper. The shutter was then set for exposure and the drum set rotating. An exposure was made, and the image of the slit, which was gradually opened and closed by the shutter, made its record on the sensitive surface. Knowing the form of the shutter, its efficiency compared with the ideal shutter would be easily calculated.

The accompanying figures show the results for a shutter working in front of the lens.

Fig. 81.

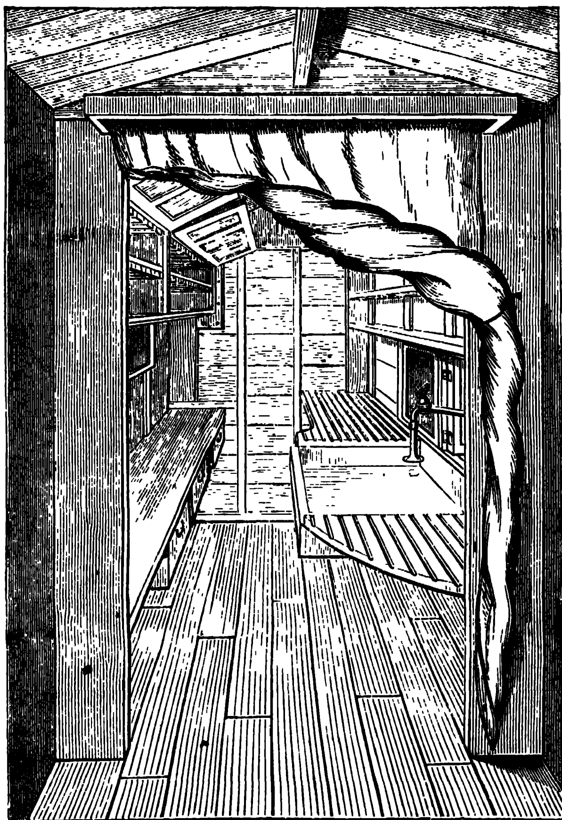


The white bars are images of the spokes of a cardboard wheel rotating in the beam of light, whose velocity is known by a syren arrangement. In the examples a quick and slow exposure of the same shutter is shown. The spokes passed through the beam of light at the rate of 140 per second. This shows that the slow exposure was $\frac{1}{23}$ second and the most rapid $\frac{1}{60}$ second.

These are what the author calls shutter diagrams. The slit began to be uncovered at a point which is shown on the

right of each figure. It gradually became still more uncovered till it reached the possible maximum. It remained thus for an interval, and gradually was covered again. The

Fig. 82.



figures show that the shutter acts more quickly at the end of the exposure than at the beginning, as might be expected.

As the shutter opened and closed with parallel wings, it is easy to calculate what its efficiency is. It will be found on calculation that it is only about half the theoretical efficiency. These diagrams were taken with a full aperture, but we can at once deduce the efficiency for any diaphragm by drawing parallel lines the proportionate distance apart of the diameter of such diaphragm compared with the full aperture. It will be seen that the smaller the aperture the more efficient the shutter becomes, and that if the diaphragm were a pin point the efficiency would be unity. The cardboard syren wheel which rotated in the beam of light had six spokes, and thirty-six holes pierced at equal intervals round the circumference. It was attached to the spindle of an electromotor which gave it a rapid rotation, and a current of air being directed through a glass tube against the holes, a note sounded, and was compared with that of a pitch-pipe. If the note sounded were E, which has 660 vibrations per second, 660 holes must have passed through the current of air every second, and this would indicate that the wheel spokes must have passed 110 times per second through the beam of light.

Figure 82 shows a very convenient dark room which was designed by De la Rue for the Transit of Venus expeditions. It was adapted for working dry or wet plates. Of course a room may be utilised, but, of whatever size it may be, it should be capable of efficient ventilation. The fumes of ammonia are pernicious when inhaled for long, and the hyposulphite bath is apt to give off sulphuretted hydrogen when gelatine plates are fixed in it.

The light which should be admitted to a dark room will be discussed in a subsequent chapter.

CHAPTER XXXIII

ON THE PICTURE

In a text-book of this class it is impracticable to enter into the discussion of all the rules which should govern the composition of a picture. It will suffice to point out a few of the leading ones which should be followed. In comparison with the painter, the photographer is sometimes under a disadvantage, in that he is unable to choose a point of view to represent some particular feature, in which everything that is objectionable to artistic feeling may be left out or modified, or in which some extraneous object may be introduced in order to give proper harmony to the picture. Thus the painter may render a distant landscape in a favourable aspect of light and shade from some particularly suitable spot, though the foreground which may be at hand may be totally unsuitable for pictorial effect. The latter he may discard for one which may be better fitted for his purpose, taking it from any other locality, providing it is not incongruous. The photographer, on the other hand, is rarely at liberty to use this artifice, unless he resort to the laborious process of printing from two or more negatives, although when the object is attained the result amply repays any labour that may have been expended. It need scarcely to be said, when combination printing is resorted to, that the greatest care is requisite to avoid incongruity, or an inartistic massing of light and shade. When confined to a single negative, there is nothing for the photographer to do but to make the best of his landscape, including his foreground. This usually entails a sacrifice to a certain extent of either one or the other, and it is the possession of the knowledge as to where the sacrifice is to end that marks

the difference between the successful artist and the mere manipulator.

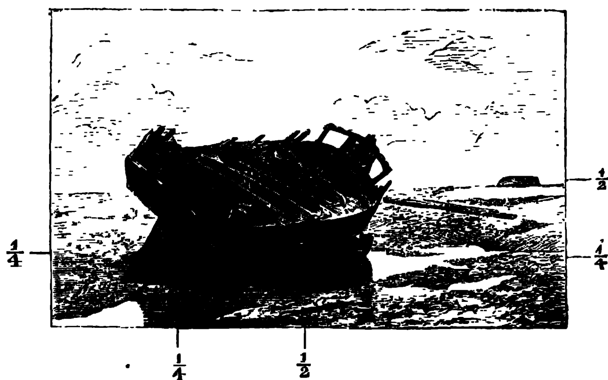
Besides focussing the object by the lens, as will be presently described, there is the focussing of the picture as a whole ; that is, the securing of the necessary harmony of light and shade. In a good and artistic photograph the object on which the subject of the picture is to be built should stand prominently out in the print, the eye should instinctively rest upon it without being distracted by other parts. Thus sweeps of shade may lead up to a more highly lighted portion in which should be the principal object, or a sweep of light may lead the eye to a dark object which then should occupy the same prominent position. In a negative as it is developed this may often be unattainable, but by judicious masking of parts during printing this harmony may generally be secured, providing the taste of the operator has been educated. It cannot be expected that an inexperienced photographer can at once form his picture, so as to give the best possible combination to the materials at his hand, until he has attained a thorough practical knowledge of chiaroscuro, and is able to translate the colours he sees on the ground glass of the camera into monochrome.

In choosing a point of view for a photograph, then, it is necessary that there should be this instinctive translation of colour into monochrome ; a knowledge of the rules which govern the formation of an artistic picture ; and a perception of the masses into which light and shade should group themselves.

Supposing that the photographer intends to make the study of an old wrecked boat lying on the sea shore ; the colour is most deceptive, the general tone being of one tint. In fig. 83 we have the example of such a study taken by Manners Gordon, a gentleman whose productions are always artistic. In analysing the work we find that he has obeyed certain rules. Thus he has made the keel to

occupy a position about $\frac{1}{4}$ way up the picture, and the nearest point of the stern occupies about a similar distance of the length of the picture. The landscape being subsidiary to the boat, he has caused the horizon line to be about $\frac{1}{2}$ way up the picture, and in order to break uniformity, he has so arranged that the boat should not be symmetrically placed in regard to the centre of the plate. The lines of the boat also make an angle with the horizon, and these are again balanced by the thwarts &c. It would have been a very easy matter to have made the picture wanting in

Fig. 83.

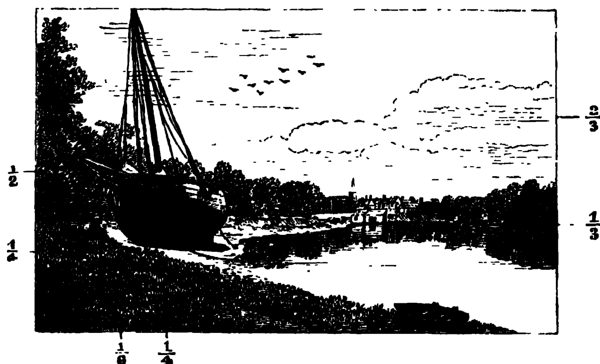


harmony by placing the camera more to the right, and causing the lines of the boat to run parallel to the horizon, in which case the boundary of the small pool of water in which it is lying would have had the same direction. The keel of the boat might also have been placed nearer the bottom of the picture, and the general mass of it have occupied a central position. In this case there would have been a symmetrical picture, the general lines running parallel to the horizon and at right angles to it, the result of which would have been that the eye would be partly satiated with it, and there would have been little variety

and much monotony. As it is, the picture, which can only be faintly represented by the woodcut, is pleasant to look at.

Instead of a boat being the object to be delineated, we may have it as an accessory to a landscape. As an example, we have a view, fig. 84, taken on the Thames by Woodbury. *The* object of interest is undoubtedly the village beyond, with its church, and middle distance formed by the trees. If the boat were taken away there would have been a large space of bare shore, unbroken by any object to relieve its monotony. The boat, however, happened to be there, and the artist has

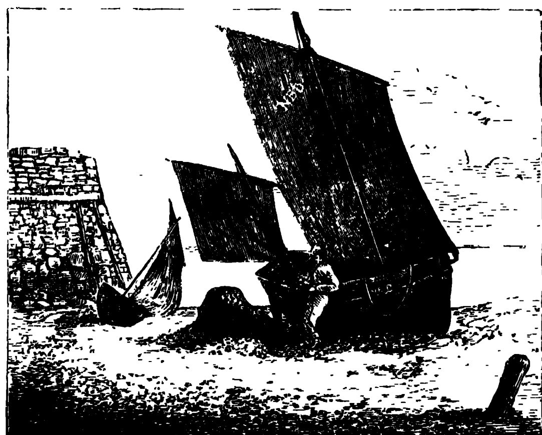
FIG. 84.



seized the chance to make a picture. Notice how it is made subsidiary to the general landscape. It does not occupy such a prominent position as in the last example. It is kept about $\frac{1}{6}$ from the edge of the picture, and the keel occupies a little over $\frac{1}{4}$ of the distance from the bottom, and the line of the village is placed about $\frac{1}{3}$ up. Were the boat brought lower down or more central, it would have appeared to have been the 'motive' of the picture. It is evident how such a picture might have been spoilt from a want of knowledge of art rules; as it is, it is a beautiful example of artistic photography.

A third example of a study of boats is given to show certain other points which are often neglected. We have here, fig. 85, a specimen of a picture that might have been readily spoilt. It should be noticed how the lines of the masts, sails, and pier are parallel, and were the figure removed from the side of the boat, and the small skiff made to lean in the other direction, the effect would have been to give the idea that the boats &c. were tumbling out of the picture, and a sense of instability would have been created.

FIG. 85.



The opposing line of the mast of the small skiff, the inclination of the figure, and the small post in the foreground, balance the general lines, and no impression of insecurity is left. The general composition, too, of the picture should be noted. The lines forming the extremities of the spars fall on the body of the skiff, while a sense of support to the outer line of the large sail is given by the post. A line drawn through the top of the post and the top of the pier would also pass approximately through the cap of the man

and the top of the mast of the skiff. The picture is then built, as it were, on diagonal lines. A slight change in the position of the camera would have altered all this. Again note that the general mass of light is opposed to the black hull of the boat, intensifying the interest with which the boat, evidently the principal object in the picture, is regarded.

The accompanying woodcut, fig. 86, taken from a photograph by Woodbury, well illustrates the treatment of an old water-mill. In this case the angle of the wall, that is, the base of the corner of the most prominent piece of masonry, is placed about ¼ way up the picture. Had it been placed lower it would have been aggressive, whilst if placed higher it would not have given sufficient solidity to the mill. The water-wheel base, the object of interest, is placed nearly centrally in the breadth of the picture, as from the subject there is no danger of symmetry, which is always distasteful. The shoot of water occupies a position central in both directions. Had it been placed much lower, there would have been a sense of a want of falling room. It will be noticed that the fall of the water naturally enhances the effect of the composition, and the light on it at once attracts the eye from the dark surroundings. If the picture be covered from the

Fig. 86.



bottom to where the board is thrown across the stream, it will be seen how a slight variation in the position of the camera might have altered the general aspect of the picture.

With some photographers forest scenes are a favourite study, and the next two examples shall treat of them. In the first, fig. 87, we have an old oak surrounded by smaller trees, the foreground composed of bracken and ferns. The base of the tree is placed about $\frac{1}{4}$ way up the picture, for if lower there would have been a feeling that there was not sufficient

Fig. 87.



ground for *it*, the principal object, to have taken firm root in, and there would have been a sense of unfitness of position. Had it been placed higher the foreground would have been too prominent, and the first idea might have been that the *raison d'être* of the picture was simply the ferns in the foreground, for those at the foot of the picture would have been out of proportion to the oak to play the part of an accessory. The distance, or what might be called the horizon line, is drawn about $\frac{1}{2}$ way up the picture, but being so broken by the shrubs and smaller

trees it is invested with no importance, and consequently need not be dwelt upon as following any particular rule. The outside of the trunk of the oak is placed ¼ way from the right-hand edge; had it occupied a more central position the picture would have appeared cut in two by it. As it is, the dark foliage behind it fills in the side of the picture, and there is no feeling that the oak is out of place. Had the foliage been light there would have been a danger that the eye might have been offended, but this is one of the cases in which the position of the camera must be made subservient to the operator. The whole force of the picture is given by the light, which breaks against the trunk of the oak; and as with the trunk, so with the branches, care has been taken to prevent any single bough cutting the picture into two divisions. Notice, too, the stability given by the straight stems of the trees, in the distance.

FIG. 88.



In the next picture, fig. 88, we have the distance, or perhaps, more strictly speaking, the middle distance as the point of interest. The horizon line is kept in the weakest part, the centre, of the picture. The trees in the foreground are so grouped that they frame the

view with dark masses, relieved by the light foliage of some of the nearer bushes and shrubs. The foreground finishes at a distance of about $\frac{1}{4}$ from the bottom. More of it would take away from the value of the middle distance, as it would place it in the weakest part of the picture, viz. centrally; less of it would have rendered the picture bald, and have cut off part of the deeper shades which are so valuable in giving the effect of distance to the stream beyond. This picture would have been spoilt had the camera been so placed as to give more top foliage, since the bough which now partially crosses the picture at about $\frac{2}{3}$ the height, would have caused an ugly division, and also the tops of the distant trees and the sky would have appeared. This latter, in views such as that under criticism, is objectionable, as patches of white give the eye an inclination to wander off towards it, and it would have been an insufficient precaution to have printed in clouds from another negative, owing to the difficulty that would exist in subduing at the same time the lights on the leaves of the near trees. As it is, the picture is in pictorial focus. By placing the stream to the right or left, the balance would have been wanting, and its general direction would have been altered to such an extent as to have given a feeling that it was a subsidiary part of the picture instead of an essential.

The next example, fig. 89, is intended to show a picture taken on the diagonal; not on an absolutely straight line, but one in which the general direction of the picture is on the diagonal. The point of interest is the extreme distance of the stream, and accordingly it is placed in one of the strongest positions in the picture, viz. $\frac{1}{3}$ way in both directions from the margins, and it contains the highest light, as seen in the water. This brilliant light is repeated in the clouds, and more faintly still it is echoed in the rocks, where it takes approximately the same form, though it is repeated in a lower tone and of different dimensions. The picture might easily have been spoilt by placing the distance in a

central position, and by arranging that the dark moss-covered rocks in the foreground should have been shifted to the side.

Fig. 89.



Had these dark masses been closely opposed to the highest light, the value of the distance would have been increased, though in their present position they are fairly well placed.

In the succeeding photograph (fig. 90) we have a capital example by Manners Gordon of a picture built up on purely artistic principles. The principal object of interest is the cottage, the value of which is enhanced by the admirable grouping of the sheep. The middle distance and background may be considered merely as accessories to support the subject of chief interest. The general direction of the picture is on the diagonal, being carried down from the chimney-top of the cottage along the bank-side to the right-hand bottom corner. The value of the composition lies principally in the light on the two sheep in the centre group, which reflects itself as it were in the whitewashed cottage front. This may be seen by imagining the front to be of the same local colour as the gable end of the cottage, or by first hiding the sheep by the finger, and then contrasting the effect produced

on the mind with that as shown. It may be remarked that the opposing lines of the clouds balance the lines of the landscape, which would not have been the case had the general contour of the clouds followed in any degree the

Fig. 90.



contour of the sky-line. In a woodcut it is impossible to give all the expression that is to be found in the photograph, but the student may gain a fair knowledge of the rules which have been followed.

As regards the introduction of figures into a landscape, it may be necessary to say a few words. It should be clearly understood that the one must be made subsidiary to the other; that is, if the portraits of the figures are required they must be made the principal objects, and the whole landscape must be made subservient to them. On the other hand, if a landscape is to be photographed, the figures, though prominent, should occupy such a position as to be subordinate to it, though they may enhance and give the 'forte' points to the picture; and above all things care must be taken that the figures compose as well with each other as with the landscape.

Robinson, in his 'Pictorial Photography,'[1] a work which

[1] *Pictorial Photography.* Sampson Low, Marston & Co.

every photographer should possess, says: 'The figure must be *of* the subject as well as *in* it, in order that unity may be preserved; it must be used with a purpose to give life to a scene, or to supply an important spot of light or dark: to give balance, or to bring other parts into subordination, by either being blacker or whiter than those parts: and that what is to be avoided is the indiscriminate dragging in of figures into scenes in which they have no business, and where they do nothing but mischief.'

We have such an example in the cut below, taken from a photograph by H. P. Robinson, called 'Blackberry

Fig. 91.



Gathering,' fig. 91. The landscape is one which is most unpromising in its aspect; the sombre bank of blackberry-bushes alone would form a melancholy, gloomy picture; but by placing these figures, as they are, some ½ way from the left-hand side, the contrast of light they offer to the deep shadow behind them at once attracts the eye, and leads it gradually up the winding broken path beyond. The spot of light, in fact, affords the exact balance required to what otherwise would be an uninteresting picture. It

accentuates everything, as it were, and gives the 'forte' point, which is such a desideratum.

Again, in this study we have an example of the value that a sky gives to a picture. It should be noticed how the lines of the clouds balance the lines of the hill. If the left-hand dark cloud be covered up, how wanting in vigour is the composition ! It will be seen how Robinson, out of such unpromising materials as a blackberry bank, a couple of figures, and a good cloud negative, has been able to build up a *picture* which is technically perfect and full of interest and repose.

In the next illustration, fig. 92, which is from a photograph by the same artist, we have a capital example of the correct

Fig. 92.



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grouping of figures to form a picture in which they are the objects of interest, and the landscape merely subsidiary, though essential. Like the typical picture by Sir David Wilkie, 'The Blind Fiddler,' this, which is named 'Holiday-making in the Woods,' is built up on a series of pyramids, the base being curved. It should be noticed how one pyramid runs into another, each corner being differently supported ; as, for example, the right-hand corner of the big pyramid is

supported by the basket, and the left-hand corner by the arm of the reclining lad. Tracing the composition all through, it will be seen the lines have been artistically kept in view and the figures posed accordingly. The straight lines of the distant trees contrast with the fall of the pyramidal lines, and give a firmness which would otherwise be wanting. The nearest object, too, is made the most distinct, whilst the darkest object, which is the figure of the boy, cuts across the highest light, giving just sufficient contrast and no more. Had the lad's head been raised higher the effect would have been to form two patches of white, from either of which the eye would have wandered by the attraction of the other. Again, leaving the main group, the two small figures lead the eye instinctively to the distant glade beyond, so that over every part of the picture we are led to some fresh beauty.

Very different are the groups so often seen as posed by many photographers. Either the heads of the standing figures are placed nearly in a line or, if a pyramidal composition is attempted, there is only one pyramid to satisfy a rule which was never intended to be rigid. In grouping there should be no uniformity; if possible, every set of figures should form a complete study by itself, blending themselves into the other sets, whilst the whole should be in harmonious lines. Again, the effect of deep shade in some figures should be made to contrast with the lighter parts of others, care being taken that no patches of light or deep shadow should be obtrusive. Above all things, in posing a group, let it be remembered that each figure is animate, and should not be made to look as lifeless as a statue. Let every member of it have a definite purpose in the group, the apparent occupation of each being in keeping with that of the others.

The next cut, fig. 93, is left for the student to find out the rules that have been followed in the composition, and also to note any improvement which might have been made in it.

We may now sum up a few of the principal rules that should be observed in the composition of a picture, though it must never be forgotten that a rigid adherence to them at all times is impossible. The great point with the photographer is to know when and how he may transgress without spoiling the treatment of his subject.

1. If the object of interest be on the foreground, its base should occupy a position of from $\frac{1}{4}$ to $\frac{1}{3}$ the height of



the picture; if it be in the distance its base should be about $\frac{1}{3}$ way up the picture.

2. In a general landscape the horizon lines should occupy a position about $\frac{1}{3}$ way from the top or the bottom of the picture; with the latter a cloud negative will probably be required.

3. It is advisable that the general line of a picture should run on a diagonal or take a pyramidal shape.

4. A long obtrusive line should never be permitted to intersect the picture; it should always be broken up as far as possible.

5. A picture should never be cut in two by a dark

object against a light background or by a light object against a dark background.

6. If the general features of a picture have a wedgelike form, care should be taken that the wedge is supported near the point, in order to give the idea of stability.

7. The general lines of a picture should be balanced by opposing lines, for the same reason as that given in 6.

8. A large patch of one approximately uniform tint is distasteful to the eye, and should be broken up, if possible.

9. The object of interest should be pictorially focussed by a general sweep of light (if it be a dark object) or of shadow (if it be a light object), thus causing the eye to fall naturally upon it.

10. Avoid monotony, in *constant* repetition whether of lines, lights, or shades, and never allow a picture to be symmetrical on the right and left of its centre. A repetition of a high light once or twice in a *lower tone* is, however, much to be recommended. See figs. 89 and 90.

As regards 8 and 9, it must be borne in mind that in the printing of the picture a great power is placed in the photographer's hand; by a judicious masking of parts he can cause pictures which would be inartistic to become merely inoffensive, and he may give an atmospheric effect otherwise unattainable by remembering that shadows in the distance tend to become lighter, whilst high lights tend to become darker. Tissue paper stretched on the back of a negative, and a limited use of the stump, will be found to be powerful aids to the production of an artistic picture.

An artistically educated photographer instinctively sees the most favourable aspect of the subject he may wish to delineate. When he perceives that he is in a favourable situation, the camera should be erected, and the minor details of the composition must be attended to. Then it is that he must exercise to the full extent his artistic knowledge. Knowing the position his principal subject

should occupy in the plate, he must note the different subordinate objects that are also seen on the ground glass of the camera. If the subject require figures to be introduced to give 'forte' points he should note where, and how, they should be arranged. He should also note the most favourable time of day for taking the view, bearing in mind that one of the chief charms of a picture is a proper massing of light and shade, which as a rule can only be secured by sunlight falling across the picture, and not coming from behind, or from the front of, the camera.

As regards the absolute manipulation of the camera there is not much to learn beyond following a few simple rules. After selecting the view, the angle which is to be taken in should be roughly measured, and the lens selected accordingly. When this is determined, the view should be brought approximately on to the ground glass of the camera. It requires a certain amount of practice to form a correct pictorial estimate of an inverted image, and it is probable by turning the head in such a position that the line joining the eyes is nearly vertical, a more correct idea can be formed than by keeping it in the usual position. At first no diaphragm should be in the lens, as the general sweep of light and shade can be better studied. When this is satisfactory, and the lines of the picture are the best that can be obtained, a diaphragm may be inserted with an aperture of the largest size which will admit of a good general focus being obtained. The object of interest must, however, be that which is most sharply defined on the ground glass, and it is sometimes advisable to sacrifice the sharpness of the other portion in order to attain this, and, when the character of the sweeps of light and shade is not as good as could be desired, it may also sometimes be necessary to adopt this artifice to secure the proper attention of the eye to that point. It is not intended to imply that a picture out of focus is more artistic than one sharply defined. Though the eye sees only one portion of a landscape at a time in

focus, the remaining portion being blurred, yet, be it remembered, the photographic print, when properly viewed, occupies the position of the natural landscape, and the same difference of focus away from the object of interest takes place naturally; and, in the photograph, as in nature, the eye may wander to the points of lesser interest, and still find a charm in the minute details.

One of the essential suppositions of perspective is, that the picture plane should be vertical and the line of sight horizontal. Nevertheless, in focussing a landscape taken merely for pictorial effect it usually does not signify whether the camera be tilted downwards or upwards, or whether the ground glass be vertical, so long as the top and bottom of the pictures are parallel with the horizontal line, though in architectural subjects, as we shall presently see, these points cannot be neglected. For a simple landscape, then, it will be found that the power of obtaining a good focus is well within the hands of the operator. From what has been already said at p. 263, it is seen that the focus of near objects is longer than that of more distant; thus, without using a diaphragm, the focus of the foreground will be longer than that of the middle distance, and this again than the distance. By using the swing-back, to cause the top of the ground glass to swing outwards, this is often secured. Again, on one side of the picture a near object may have to be represented; by using the horizontal swing, it may often be brought into focus. By the use of the vertical and horizontal swings together, it is sometimes possible to employ a much larger diaphragm than could otherwise be done. In landscapes this is often important, as a large available aperture to the lens means short exposure; and where the operator is exposed to the caprices of gusts of wind, the success of a picture is often dependent on the rapidity of exposure. As regards the tilting of the camera, latitude is allowable in landscape work. When the swing-back is used it is better to have a tilt downwards than to

keep it level, as by so doing the plate is kept more nearly vertical than would otherwise be the case. A tilt upwards exaggerates the distortion, and it is better to raise the board carrying the lens of the camera than to give it a tilt in this direction. Raising the lens board means taking off a portion of the foreground. This has the same effect as tilting the camera, though without causing the direction of the axis of the lens to be altered. As a general rule, however, tilting should be cautiously and sparingly used, otherwise it is apt to suggest that there is something wrong about the picture.

When the best general focus has been obtained by the above artifice, the diaphragm should be inserted so that the necessary amount of sharpness may be obtained, recollecting that the brighter the image, the greater will be the vigour of the resulting negative. When great contrasts in light and shade are in question the introduction of a small stop may sometimes be advisable, as will be evident by consulting the next chapter.

In focussing architectural subjects, where it is of importance to preserve the parallelism of vertical lines, the sensitive plate must *always be kept in a vertical plane.* In case the axis of the lens has to be tilted the swing-back must be used till this is attained. When this vertical plane is not adhered to we shall have the vertical lines which are parallel in nature converging in the picture. If we look at a cube lying on a horizontal plane the feeling to the *eyes* is that the vertical lines are parallel (perhaps because the most natural position for natural movement of the axes of the eyes is in a horizontal rather than in a vertical plane); if, however, we tilt the cube the impression at once vanishes, and they will seem to converge. Hence to give the idea to the mind that an object is standing on a horizontal plane, the vertical lines must appear parallel to the eye, whether seen in nature or seen in a picture. Now, it can readily and easily be demonstrated that by tilting the camera with-

out using the swing-back, vertical lines must converge, hence the resulting picture would be untrue. It will perhaps aid the student in regard to the use of the swing-back to remember that for theoretical purposes the lens, whether its axis be tilted or not, may be replaced by a pin-hole in an opaque card, and that the image received through the pin-hole must be theoretically correct when received on a vertical plane.

As regards the exposure to be given to a picture there is one golden rule to follow: 'Expose for the shadows and let the lights take care of themselves,' that is, the detail in the shadows must be developable.

During exposure something may be done to give harmony to the negative by shading the lens with a piece of blackened card from those parts, such as the sky and clouds, which are most quickly impressed on the plate.

As regards portraiture the variations in lighting that can be produced in a well-appointed studio are so numerous that it would be impossible to treat of them in a limited space. For outdoor portraiture an angle of a wall facing the north with a background formed by a blanket is suitable for producing pictures that can be vignetted.

Indoor portraiture can be attempted where a window with a northerly light is available, and where white screens are at hand to lighten up that portion of the face which is in shadow. Ordinarily the principal light should make an angle of about 45° with the vertical and horizontal planes which intersect in the axis of the lens.

The student should refer to 'Pictorial Photography' for a comprehensive description of what to do and what to avoid. The rules given for landscape photography, however, in a great measure apply, particularly paragraphs 3–5, 7–10.

CHAPTER XXXIV

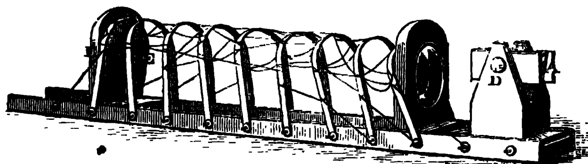
PHOTO-SPECTROSCOPY

ONE of the branches of science into the service of which photography has been impressed is that of spectroscopy, and the aid it has given dates from nearly the early days of the daguerreotype. In the researches at present made with the spectroscope it plays such an important part, that a rather detailed description of the apparatus necessary and the methods employed will be given.

Photo-spectroscopy, however, has two aspects: in one it is the study as to the sensitiveness of compounds to the influence of different portions of the spectrum; in the other the study of the spectrum itself. The first may be considered an essential preliminary to the second, and will therefore be examined first.

In the loan collection of scientific apparatus at South Kensington is exhibited the instrument with which Herschel

FIG. 94.



made his classic researches on various substances which were acted upon by light. His experiments were undertaken before the days of the collodion process, and his *modus operandi* consisted in giving washes of one or more solutions to paper, and then submitting the sensitised paper to the solar spectrum. The accompanying diagram, fig. 94,

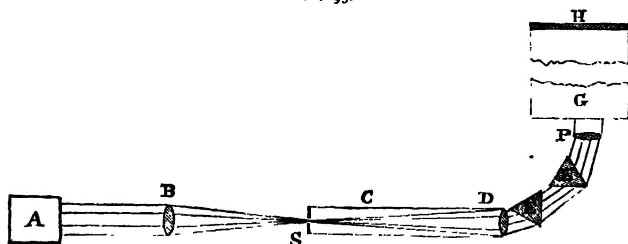
gives an idea of the prismatic arrangement he adopted. A is a flint-glass prism, capable of turning on an axis, D; B a lens of about 24-inch focal length; C the screen on which the sensitive paper was placed. The sunlight was reflected by a mirror into the prism, the image of the sun after passing through A was elongated into a spectrum, and brought to a focus on C by means of the lens B. One portion of the spectrum was caused to fall on the line, E F; the particular ray being found by examining the spectrum by means of a piece of cobalt glass, which cuts off all rays excepting two. The cage was covered with a black velvet cloth. It will be noticed that no slit was employed, but that the spectrum was really formed by a series of overlapping images of the sun. The spectrum was thus of necessity an impure one, and in the results obtained with it this has to be taken into consideration. For a detailed account of the experiments carried out by Sir John Herschel, the 'Philosophical Transactions of the Royal Society' should be consulted, and also 'Hunt's Researches on Light.' The registration of the Fraunhofer lines of the solar spectrum was effected by Becquerel and Draper with an instrument similar in general principles to that which will presently be described. Both of these eminent physicists employed the Daguerrean process with the greatest success in these researches. The latter performed the feat of registering the lines in the least refrangible portion of the spectrum by the reversing action of the red rays, of which a description will be given subsequently.

An apparatus that will answer the purpose for a student will now be described. The great essentials are good prisms and a collimator of fairly long focus. These may be purchased separately from an instrument-maker, and fitted up by the operator, if he be at all handy with ordinary carpenter's tools. Thus the collimator tube may be supported in a cradle, and the prisms mounted on a block of smoothly planed wood, or a slate slab, so arranged that the axis of

the lens of the camera is of the same height as the centre of the prisms, as is also the axis of the collimator.

The accompanying arrangement shows the manner in which a temporary photo-spectrum apparatus can be fitted up. A is a heliostat, throwing the sun's rays into the condenser, B, by which an image of the sun is formed on the slit of the collimator, C. The lens, D, of the collimator is so placed that its equivalent focus falls accurately on the exterior of the slit. This should be obtained by trial, and it is very

FIG. 95.



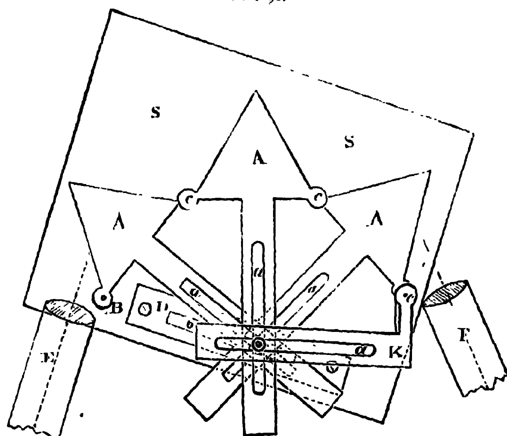
advisable that the slit arrangement should be attached to an inner tube, which can slide in that to which the lens is attached. The rays proceeding from the illuminated slit travel in such a manner that when certain requirements, which will be entered into presently, are satisfied, the lens of the collimator is perfectly filled, or at all events the rays of light form a central disc on the lens, D. The light then travels to the prisms, E, E, by which it is refracted and dispersed, and then it reaches the lens, F, of the camera, G, by which lens the spectrum is thrown on the plate, H, where it is focussed. As difficulties frequently arise at first in the adjustment &c. of the apparatus, a few hints may not be out of place. In order to secure good results the focal length of the condensing lens, B, when divided by its diameter, should never exceed the length of the collimator when divided by the effective aperture of its lens. Should it do so, it will be seen that the collimating

lens will be more than filled, and reflections from the sides of the tubes might interfere with definition. Again, it is useless to have prisms which cannot receive all the rays proceeding from the collimating lens. Their height should, therefore, be at least equal to the effective aperture of the collimating lens, and the faces should be longer, since they are placed obliquely. In all cases the centre of the mirror, the axis of the condensing lens and of the collimator should be in one straight line. To effect this, it is better at first to remove the condenser from the train of apparatus. The image of the sun, when thrown on the slit, should give a bright diffused line occupying the *centre of the collimating lens*, D. The position and height of the heliostat must be changed till this is obtained. The condensing lens, B, may now be inserted and moved till the rays of light form a circular disc, filling the centre of the lens, D, when a sharp image of the sun is thrown on the slit. When this is obtained the prisms may be placed in position. By the aid of an ordinary small telescope the angle of minimum deviation may be obtained. Suppose it is required to photograph the portion of the spectrum about the line G. The prism would be placed roughly in position, and that line would be observed. It would be found that by turning the prism in one direction, the line would appear at first to travel in one direction, but that when a certain point was reached it would begin to travel in the opposite direction. The position the prism occupied when the change in direction of the apparent motion of the line took place would be the position the prism should occupy, in order for that particular ray to be refracted in the angle of minimum deviation. It is often insisted upon that this angle is of supreme importance, but it can be shown that when a collimator is used, and not a distant slit alone, the resulting spectrum will not give erroneous impressions. It must be admitted, however, that the angle of minimum deviation is a position which is convenient if not necessary.

After the first prism is adjusted, the second and other prisms may be adjusted in like manner. When once they are fixed the positions can be marked by lines if on a slate table, or by small guides screwed into the wood if a board be used. The camera should be finally placed in position so that the ray for which the prisms have been adjusted should occupy the centre of the focussing screen or sensitive plate.

Another contrivance [1] for always securing the minimum angle of deviation is shown in the accompanying diagram.

Fig. 96.



Cut out, in stout card or brass, pieces having the form A A A, also D and K. Care must be taken that the bases of the triangles are of uniform lengths, and slightly longer than the base of the prisms, which should be of uniform angle, and preferably of equal size. D should be let into the board S S, so that its top surface is flush with it, and there should be a groove cut beneath the slot, *b*, to allow a pin, of a diameter

[1] The principle of it is due to Mr. Browning, the optician, but we first saw this easy adaptation of it to ordinary work in the laboratory of Dr. Huggins.

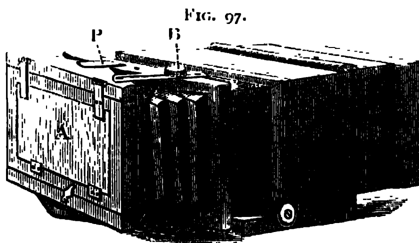
equal to that of the slot, to travel along it. The slots *a a a* in A A A and K are also placed over the pin. The first triangle is attached to the board, S, by a pin at B. The remaining triangular portions, and also K, are attached to each other at *c c c*, and are free to move over the board S. The axis of the collimator E is placed at right angles to the slot *b*, and, by touching K, the arms from the triangular portions move about the pin, the slots, *a a a*, guiding the motion at the same time the parts move separately about *c c c*, and the whole system turns about B. It will be seen by this that the base of a triangle moves through twice the angle of the preceding one, as also does K. The direction of the line joining the point in K, answering to the middle point of the base of the triangle, and the middle point of the base of the adjacent triangle, determines the position of the axis of the lens, F, of the camera. Such a board may be used as a pattern by which to set the prisms for any particular part of the spectrum, or the prisms themselves may be set on the triangular portions, provided the board, S S, be perfectly plane, and that precautions be taken to raise by obvious means the prisms to the same level, and to cause the triangular patterns to be so adjusted that there shall be no deflection owing to their arms being at different heights on the pin. It will be found that two prisms of 60° and two of 45°, or three of 62°, will be the greatest dispersion that can be employed, unless special arrangements are made. As a guide to the length of spectrum that can be photographed at one time, it may be stated that with a lens to the camera of 120 centimetres focus, and using one ordinary flint prism of 60°, a photograph of about 10 centimetres is obtained; and with the same camera and two prisms of 60° the length of spectrum is about double.

To focus the lines accurately is somewhat difficult, for it will be found that the focus of the violet rays is shorter than that of the red.

The accompanying figure shows the kind of camera that

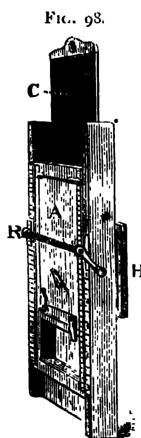
the writer designed and employs. It is made by Meagher. It is separated into lengths varying from 6 inches to 18 inches, and is thus adapted to a lens of any focus from 9 inches to 6 feet. The swing-back enables the plate to

FIG. 97.



be tilted to any angle up to 40° in a vertical plane. For registering many spectra on the same plate a special slide is arranged, as shown in fig. 98. The full plate which it can take is $7\frac{1}{2} \times 5$ inches, and the rack and pinion motion enables it to be raised a quarter of an inch at a time, thus allowing at least 15 exposures to be taken on such a plate. When the length of the spectrum is small, an inner frame to carry a quarter plate may be used, allowing some 10 exposures to be made on the same plate, a matter of no small convenience.

FIG. 98.



It is usually prescribed that the focus should be obtained by placing a transparent glass plate in the place of the ground glass and viewing the spectrum by a high-power magnifying lens. This latter should be attached to a sliding tube, so that when the end of the tube is placed against one surface of the glass plate the other surface immediately opposed should be in the plane of its focus. By this means the rays which have to be focussed on the inner surface of the plate can be viewed by the magnifier, and the plate of glass moved backwards and forwards by the screw motion of the camera, till the lines appear sharply defined to the eye.

Theoretically, this is a perfect method, but practically it fails if two portions of the spectrum which are far apart have to be photographed at one operation, for the necessary inclination of the surface of the glass away from a plane perpendicular to the axis of the lens (the deviation being effected by the swing-back) is so great that the axis of the magnifying lens is thrown completely out of the direction of the rays of light, and there is necessarily no image observed.

Unless a microscopic arrangement be employed, it is better to obtain a fair focus on very nicely ground glass, or on a plate coated with very fine gelatine bromide emulsions, and then to make the final adjustments by trial.

A good method of obtaining the correct distance of the collimating lens from the slit may here be indicated by means of an eyepiece. Make an ink mark or a scratch on a piece of glass, place it against the eyepiece, which should be surrounded by a draw-tube, and focus the ink mark or scratch, which should be next the eyepiece, by altering the draw-tube. Now place the draw-tube of the eyepiece against the jaws of the slit (which would be rather widely opened), and view some *distant* object through the collimating lens. When this appears quite sharply defined, the definition being obtained by altering the distance of the slit from the collimating lens, this adjustment is complete.

In the case of a lens only partially corrected, the focus may vary. In one position the image may appear perfectly sharp but surrounded by a blue fringe, and in another by a red fringe. When the most refracted rays are to be photographed, that focus should be chosen in which the red fringe is seen; when the least refracted, that in which the blue fringe is apparent.

It must be recollected that the greatest accuracy in all these points is requisite in order to obtain the best results.

When other than the sensitive salts of silver are to be examined, a single prism will suffice for the dispersion, using a camera lens of about 18 inches focus.

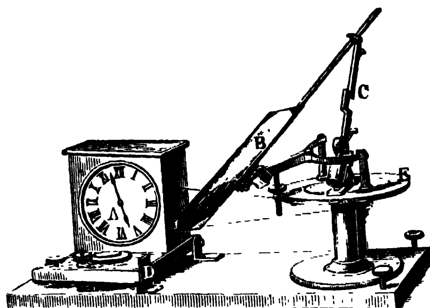
It is better then to open the slit to such a degree that the Fraunhofer lines broaden out. One or two distinguishing lines, such as the H and *b* lines, will still be traceable, and from these, and by a comparison with a picture taken on a silver compound, with a more closed slit, the limits of the spectrum impressed on the sensitive salt under consideration may be accurately obtained. For, obviously, when the slit is say a millimetre wide, there is but little impurity in the spectrum. With this apparatus, as in that above, it is advisable to employ a condenser.

We have hitherto been supposing that sunlight was to be used as the source of illumination, but sunlight is not a necessity. Skylight will answer for investigations on the salts of silver, as will also an ordinary gas jet, or an incandescent lamp. In fig. 95, instead of employing B to focus the sun's rays, it may be employed to focus on the slit any other source of light; an electric arc light may be employed, using the violet in the positive pole as the part focussed on the slit, but for delicate work this is somewhat difficult to employ, as there is a series of carbon bands in the violet and ultra violet, which may be misleading. To ascertain the positions of the different parts of the spectrum, a spectrum should be photographed of the light from burning magnesium wire, or of the base of the blue flame of the gas jet or of a candle. Either of these will give lines, the positions of which are known, and with which the photographed continuous spectrum may be compared.

For the student who uses sunlight or skylight, an ordinary mirror may be employed. It is preferable to use one silvered on the front surface, as the double reflections are thereby avoided. The mirror should be of carefully selected patent plate, and be silvered on the best surface, and the silver should be brought to a fine polish. It is convenient to use a heliostat when sunlight is to be employed, and the form given in the accompanying figure, designed by Stoney, answers well with a little care.

A is a small French clock, round the drum of which, and also round a small wheel fixed on the instrument, passes a cord. B is a mirror, held in position by a rod which slides in a pivoted socket at the end of C. C is attached to a part which answers to the polar axis ir an equatorially mounted telescope, and it is to this polar axis that the driving-wheel alluded to is fitted. It will be noticed that the clock stands on a board which is fastened to the base board of the entire instrument. A level is fixed on this clock board, and the plane of the board can be caused to make a certain small angle with the base board

FIG. 99.



by means of a screw adjustment. The amount of 'tilt' is indicated by the arc D. When the clock stand is levelled, a certain diminution or increase of angle to the vertical can be given to the polar axis. The instrument is placed in position as follows: The polar axis is made to point to the pole, any small difference (say of 2 or 3 degrees) of latitude being adjusted by a small arc D. When the clock stand is levelled the polar axis will then occupy the required angle with the horizon. The method of securing a true north point for the axis will be apparent when the instrument is examined; for by making E, which is a circular annulus graduated to hours, into a sundial, a north point

approximately correct can be found. C is then placed at such an angle that the image of a small round hole, bored in a brass disc attached to its top, is seen to shine on a small ivory screen attached at its lower part. The graduated annulus, to which B is also attached, is then moved till the sun shines in any required horizontal direction. Vertical motion is given to the beam of light by using the screw shown in the figure.

Another form of siderostat will be found in chap. xxxix. treating of Celestial Photography.

For photographing with the prismatic spectrum a typical one is that employed by Lockyer for his researches on the solar spectrum as sketched in fig. 100.

A is a vertical slit, whose exterior face is covered by a plate, capable of moving horizontally, in which two or more apertures are cut *en échelon*, the top of the lower one being in accurate continuation of the bottom of the upper one, and so on. When the top aperture of the movable plate is in front of the slit, only the top part of the slit is uncovered, and when the bottom aperture is in front of the slit the bottom part of the slit is uncovered. At B is a rack and pinion, which is used to adjust the distance of the slit from the collimating lens, inserted at the other extremity of the tube C. At D is a train of prisms (the number in which can be altered at pleasure), set to the angle of minimum deviation for the mean of the rays which it may be desirable to examine. E is a camera, some 6 feet long, furnished with a lens of that focus, and the usual means of focussing. At F is inserted the dark slide, capable of containing a plate 6 × 2 inches. The spectroscope and camera are rigidly connected one with another, the prisms and collimator, C, being fastened to an iron plate, T, supported on a solid pillar, S. This completes the photo-spectroscopic arrangement. In order to compare the spectrum of a metal with that of the sun, Lockyer adopted the arrangement shown. K is an electric lamp, between the points of which the metal

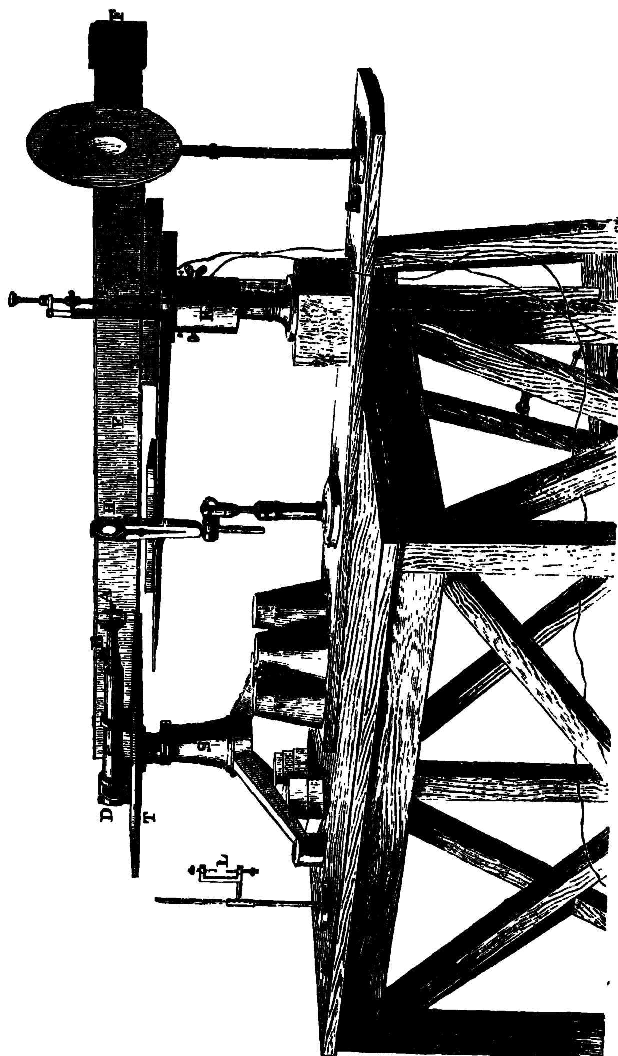
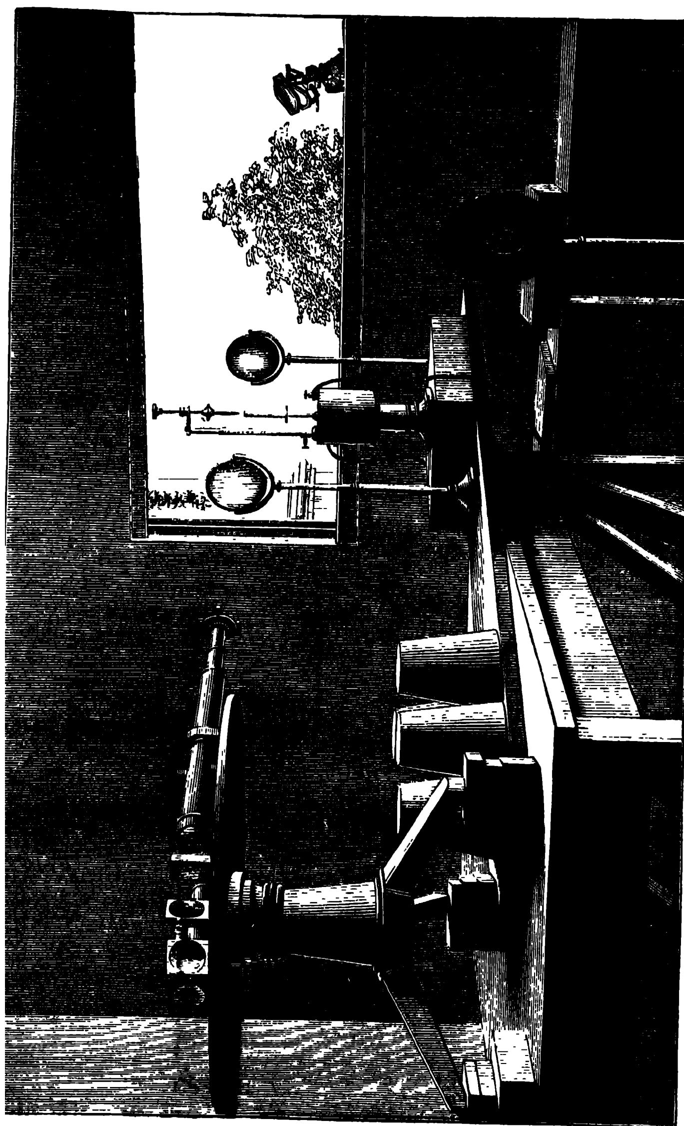


Fig. 100.

to be examined is volatilised by means of the electric current passing between them. The points are so placed that the interval between them lies in a continuation of the axis of the collimator C. At H is a small lens, the distance between A, H, and P being so arranged that A and P are conjugate foci of H. In some cases the place of the lamp is occupied by a Ruhmkorff coil, and the metal volatilised by the heat of the spark. G is another condensing lens on to which the solar rays are thrown by means of a heliostat, and placed at such a distance from A that its principal focus—the focus for parallel rays—is at P. By this arrangement the lens H will throw a perfect image either of the sun, or of the electric arc, on A. This arrangement of the instrument is shown in fig. 101.

When the portion of the solar spectrum required has been accurately focussed on the plane to be occupied by the sensitive plate at F, fig. 100, the top half of the slit is uncovered, the metal to be examined brought between the carbon points, P, and the current caused to pass between them. The spectrum of the volatilised metal falls on the sensitive plate, and impresses itself in from half a minute to half an hour, the time varying according to the portion of the spectrum worked with. When sufficient exposure has been given, the carbon points of the electric lamp are separated, the bottom half of the slit uncovered (the top half being at the same time of necessity shielded from the light), and an image of the sun allowed to fall on it. As everything remains in the same position, excepting the part of the slit left open, the corresponding portion of the solar spectrum falls on the sensitive plate, but in this case immediately above that of the metal.

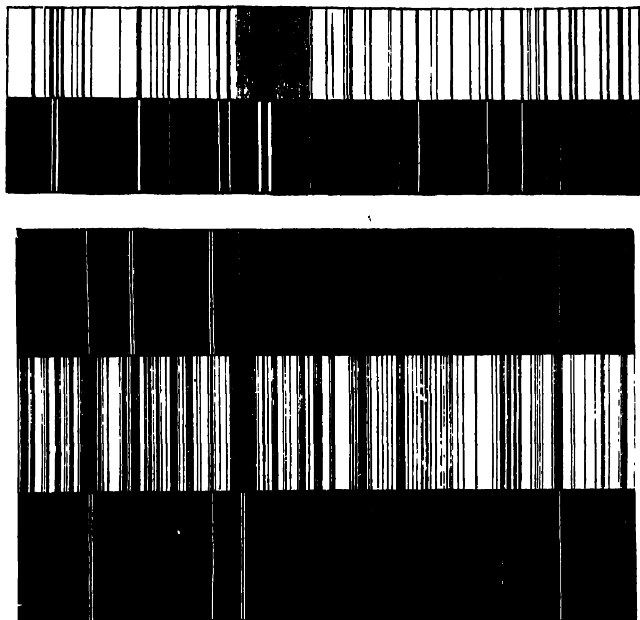
It will be seen that it is quite possible to compare the solar spectrum with two metals by increasing the number of apertures *en échelon* in the sliding plate to three, if the solar spectrum be taken with the middle of the slit. Two examples of the photographs obtained by Lockyer are annexed, fig. 102. The first shows the coincidence of



some of the bright lines (near H) of the spectrum of iron, with the absorption lines in the solar spectrum, and the second shows a similar comparison between calcium, aluminium, and the sun.

The materials which are used in the spectroscope or for the reflectors is a matter of some importance. Glass is

FIG. 102.



usually employed for the prisms and lenses, but for studying the ultra-violet a quartz train is a desideratum, since glass absorbs the extreme rays of that portion of the spectrum. W. A. Miller studied the absorption of different transparent solids, and although undertaken at an early date in the history of photography the results are even now useful. The following are some of the results obtained by Miller:

Name of Substance	Thickness in Inches	Termination of Spectrum	Relative lengths of Spectra	Remarks
Ice	About 5	170·5	74·0	
Diamond . .	·032	155·5	59·0	
,, ...	·017	159·5	62·0	
Quartz . . .	·16	170·5	74·0	
Fluorspar . .	·17	170·5	74·0	
Rocksalt . . .	·75	159·5	63·0	
Silver nitrate . .	·75	106·0	9·5	Saturated solution
Iceland spar . .	·35	160·0	63·5	
Faraday's optical glass	·54	101·5	5·0	Pale yellow
Flint glass . .	·68	105·5	9·0	
Window sheet glass .	·07	112·5	16·0	
Hard Bohemian glass	·18	114·5	18·0	
Plate glass . .	·22	111·5	15·0	
Crown glass . .	·74	106·5	10·0	Greenish

He used a quartz train for the purpose of his investigation. The line B in the extreme red is 84 on his scale, and the line H in the extreme violet 100. In every case the commencement of the photograph was 96·5 near G on his scale, silver iodide being the sensitive salt employed.

Dr. W. A. Miller also investigated the reflected light from different polished surfaces. Of metals and alloys he tried the following: platinum, gold, silver, mercury, lead, copper, tin, cadmium, zinc, aluminium. For photographic rays no judgment could be formed of the perfection of the reflecting power from the colour of the metal. The following is a summary of his results:

Gold.—Reflects all rays, even the most refrangible, equally.

Spectrum extends from 96·5 to 170·5.

Lead.—Similar to gold, some parts of the spectrum being more strongly reflected.

Spectrum extends from 96·5 to 170·5.

Silver.—Impressed spectrum strong, from 96·5 to 112·5,

a break for 1·5 of the scale, and then recommencement, continuing to 159·5 of the scale.

Mercury.—Strong at each end of the photographed spectrum, but weak in the middle; extent, 96·5 to 159·5.

Platinum.—Same as mercury, but less intense.

Zinc.—Same as mercury, but less intense.

Aluminium.—Same as mercury, but less intense.

Cadmium.—Same as mercury, but less intense than the last three.

Copper.—Deficient in strength for last half (most refrangible) of the spectrum ; extent, 96·5 to 159·5.

Brass.—Same as copper, but weaker.

Steel.—Intense spectrum ; extent, 96·5 to 159·5.

Speculum metal.—Intense in least refrangible half of the photographed spectrum, but weak in the most refrangible half ; extent, 96·5 to 159·5.

At the present time diffraction gratings, used by reflection, are much employed. If the grating be flat, the collimator and camera remain the same as when prisms are employed, and it is well that the plane of the grating should be at right angles to the axis of the camera lens. A special form of apparatus is employed for this purpose. It should be noted, however, that the brilliancy of the different spectra exhibited by different gratings is by no means always what theory would give, and it may be that some gratings used by reflection cut off portions of the spectrum either by want of reflection from the metal employed or by peculiarity in the ruling. Gratings may be obtained with lines varying in number per square inch from 3,000 to 17,000 or even more. The advantage of a grating is that the wave lengths of different lines can be determined from photographs if it be placed as indicated above. The violet and

ultra-violet do not occupy the inordinate length which they do in a prismatic spectrum. Nor are the red and infra-red condensed as they are when prisms are employed. Excellent copies of transparent gratings have been made, and these are used by transmitted light, and are perhaps more accurate in giving the true illuminating value of the different parts of the spectrum than are the reflection gratings.

Concave gratings have been introduced by Roland, and the advantage with them is that they need no camera lens nor collimator. The slit is focussed by the concave surface and there is no loss of sharpness through want of achromatism of the lenses employed.

It should be noted that the earliest published photograph of a diffraction spectrum, at all events of any scientific value, was due to Dr. H. Draper. He first published it in England in the 'Phil. Mag.' for Dec. 1873. The lines are not absolutely defined, but still sufficiently so to be of value.

As to the material of which reflection gratings are made, the table on pp. 329, 330 will show of which metal they would be best made for photographic purposes.

CHAPTER XXXV

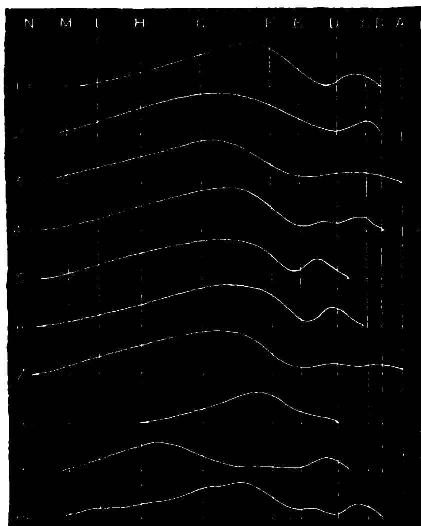
ORTHOCHROMATIC PHOTOGRAPHY

We now come to the effect of certain dyes on sensitive salts of silver, but as the salt to which the application is most generally made is the bromide, the remarks that will be made will be principally applied to it.

In 1873 Dr. H. W. Vogel, of Berlin, found that the addition of certain dyes, such as corallin, magdala red, gave more than one, or changed the position of the, maximum of sensitiveness in the spectrum. Vogel experimented with the

collodion processes, since at that date the newer gelatine process was not workable. The application to gelatine plates, however, was a natural outcome of this, and who first applied it is doubtful. Vogel, Eder, and the writer all experimented in this direction. Eder, however, carried out a very extensive series of experiments with different dyes, and gave a very complete discussion of each. As a matter of fact, the

FIG. 103.



No. 1 is the effect of Hoffmann's violet, gentian violet, methyl violet, and acid violet. No. 2 shows the effect of benzaldehyde green, ethyl green, methyl green, and other varieties. No. 3 is iodine green. No. 4, cyanin blue. No. 5 is eosin and the members of the eosin group. No. 6, rose Bengal and ammonia. No. 7, cœrulein. No. 8, chrysanilin. No. 9, eosin and silver chloride. No. 10, eosin and cyanin.

two typical dyes which are at present most employed are eosin and cyanin blue.

The above figure[1] will give an idea of the relative

[1] Taken from a paper read before the Society of Chemical Industry, June 30, 1887, by C. H. Bothamley, F.I.C., F.C.S.; it is a reproduction from Eder's paper.

sensitiveness to the different parts of the spectrum of a gelatino-bromide plate to which various dyes have been added.

When collodion is used it is easy to employ an excess of silver nitrate, in order that when possible the dye may form a coloured compound with the silver, which is sensitive to light. With the gelatine process this is not so easy, though it can be effected by an artifice (the reason why the silver cannot be in excess in a gelatine emulsion has already been pointed out). Eosin and the variations of eosin, such as erythrosin, will each form a compound with silver nitrate, which in a neutral or acid solution of the former is precipitated by the addition of a solution of the latter. This precipitate can be washed by decantation till all traces of silver nitrate are eliminated. This solid organic compound of silver thus isolated dissolves readily in a very dilute solution of ammonia, and can in this manner either be added to the gelatine emulsion, or a prepared plate can be soaked in it and dried. Plates prepared in this manner are exceedingly sensitive, though some writers assert that they are not so sensitive as when prepared in the following manner.

In chapter xi. p. 105, on the making of emulsion by the ammonia process, if dye be added to a small extent to the bromide solution so that it is of a salmon colour, and the precipitation takes place in the presence of the dye, it appears that the dye combines with the silver bromide, forming a double compound which gives a film which is very sensitive in the green.

Another plan, which is very usually adopted to convert an ordinary plate into one which is sensitive to the green and slightly in the yellow, is to make a solution of the dye in ammonia and to bathe the plate in it, and then to allow it to dry. The following formula was given by Dr. Mallmann :

The plates having been dusted are placed in

Ammonia	2 parts
Distilled water	200 parts

Afterwards the plates are dipped in a bath made as below:

Erythrosin or eosin (1 : 1000 of water) .	25 parts
Ammonia	4 parts
Distilled water	175 parts

They are kept in this for 1 minute to $1\frac{1}{4}$ minute, and are drained on a porous tile and dried in the dark.

The addition of a few drops of a saturated solution of cyanin blue to the above carries the sensitiveness of the plate further into the red of the spectrum (see No. 10,

FIG. 104.

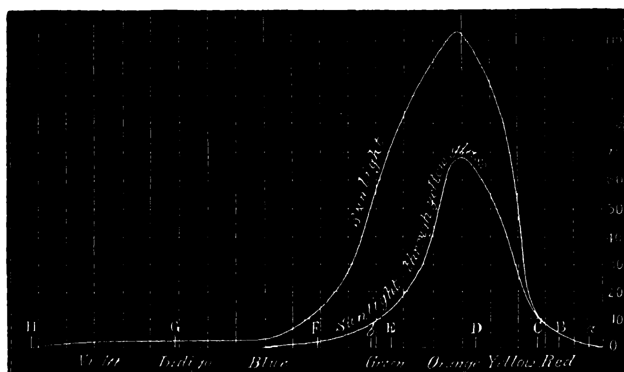


fig. 103), and was the combination first made, he believes, by the writer in 1882.

As to the practical use of the addition of these various dyes something must be said.

If we take sunlight and pass it through one or two prisms and view it on the screen, we find that the yellow region is by far the brightest, and the blue and violet region the feeblest in luminosity. Yet it is these latter regions which have the principal effect in photography on ordinary plates. The above curve of the luminosity of the spectrum of sunlight is taken from a paper by the writer which

appeared in the 'Philosophical Transactions' of the Royal Society for 1887, and is for a sun of medium altitude. The height of the ordinate measures the luminosity at any particular part of the curve. From this it will be seen that the greatest effect on the eyes is produced by the rays which lie between the green and the yellow. If, therefore, a photograph can be taken with some body which is more sensitive to this part of the spectrum than to any other, manifestly it will give a truer effect of the illumination of the object seen than if the blue rays are the active ones. Thus in a yellow flower or in a sunset sky there is very little blue, but a great deal of yellow, the latter being very luminous. If these two objects be photographed, one with a compound which is most impressed by the yellow, and again with one which is most sensitive to the blue, it is evident that the former will give a more truthful monochrome print than the latter.

For an exact representation in monochrome, perfect truth can only be attained when the curve of sensitiveness of the compound to the spectrum follows the curve of luminosity of the spectrum, and at present such a compound has not been, nor, if an opinion may be expressed, will it ever be, found, but an approximation may be made by an artifice.

Suppose we look through yellow glass at objects lighted by sunlight, the blue will be nearly cut off and the violet entirely, but the general effect of a coloured landscape or drawing, so viewed, will have the same general effect of illumination though the colours themselves will all be yellower. If we take the illumination of the spectrum transmitted through yellow glass it will be of the character shown in fig. 104 in the lowest curve, from which it will be seen that the place of maximum illumination is very little changed, though the violet and blue are absent. If we attempted to take a photograph through such a yellow glass on a wet plate we should get no effect, though if we used a gelatine-bromide plate, which is sensitive to the green, an impression would

be made, but the predominating colour value would be in the green. If, however, we employ a plate dyed with cyanin, erythrosin (one of the eosin group), or a mixture of the two, a reference to fig. 103 will show that a strong effect will be made by the green and the yellow, so that a photograph may be taken through a yellow glass which will fairly represent in monochrome the illuminative value of the different colours.

If a landscape be taken with these dyed plates (which have been named isochromatic or orthochromatic) without yellow glass intervening, there is very little difference between the result and that obtained on an ordinary plate, the reason being that the objects reflect a large proportion of white light, and that the blue light in this reflected light is that which is most effective (see fig. 103). If, however, a yellow glass be placed in front of the lens, the photograph will differ considerably in appearance. The blue of the sky, for instance, in the resulting print, will be rendered a grey instead of white, whilst a white cloud will be white. The greens of the trees and grass will be more harmonious, and so will any yellow object which may be in the view. Mr. B. J. Edwards has introduced a very neat arrangement for introducing a yellow screen between the object and the plate. With a doublet-lens, where Waterhouse stops are used, he fastens between two thin cards, in which is cut a circular aperture, a thin sheet of gelatine dyed with aurine or some other similar colour. The film is so thin and even that no serious deviation takes place in the rays of light passing through the lens, when such a card takes the place of the stop. The writer adopted the plan usually recommended of placing in front of the lens a piece of orange glass, but only one piece out of some twenty was sufficiently true in its surface to be capable of being utilised, whereas by employing Mr. Edwards's plan no difficulty was experienced.

For copying coloured pictures, as already hinted, these orthochromatic plates are excessively valuable, always taking

the precaution of using some yellow medium as indicated above. The exposures have to be more prolonged than when a plate without the screen is employed, since the most effective rays are cut off. The increased exposure may vary from 6 to 60 times that usually required, the time depending on the sensitiveness of the combination.

The theory of the effect produced by the addition of dyes to sensitive salts of silver may be summed up as follows:

1. There may be an organic salt of silver formed, either by the combination of silver nitrate or of silver bromide (or chloride) with the dye; in the latter case, the formation of the compound is aided by the solubility of the bromide (or chloride) in ammonia. Such an organic salt of silver may be sensitive to rays of the spectrum to which the inorganic salt is insensitive, or it may only exalt the sensitiveness of the inorganic salt for some particular part of the spectrum.

2. If the dye is fugitive, *i.e.* one that rapidly fades in the light (as cyanin does), the faded dye becomes oxidised, and the oxidised body acts as a nucleus on which the silver reduced by the developer is deposited.

Vogel has called some of these dyes *optical sensitisers*, and explains the term by stating that where the dyes absorb the light, there apparently a sort of secondary action takes place. This is not an explanation which our present knowledge allows the writer to admit. It is believed that the first given explanations are more consistent with the theory and fact than the latter. The locality of the spectrum in which the dyes may be expected to increase the sensitiveness of the plates can be readily found by examining the absorption spectrum of the dyes or their compounds. Where the light is absorbed, there the sensitiveness may be increased. It has been stated by some writers that there is no exact coincidence between the two, but only a general coincidence. By careful examination, however, and by taking proper

precautions, the writer has found that the coincidence between the localities of absorption and chemical action in the spectrum is exact, and does not follow a quasi-law enunciated by Kundt, which can scarcely, as yet, be fully accepted, and which would have made only a general coincidence between absorption and chemical action possible.

Thus, in every case of chemical action taking place by the spectrum, it may be laid down that the body acted upon absorbs in the same localities. This is a law which *must hold good*, since it is part of the law of the conservation of energy.

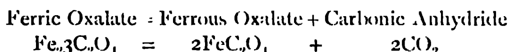
CHAPTER XXXVI

ACTINOMETRY

AMONGST the earliest methods of comparing the chemical energy of different lights is that known as Bunsen and Roscoe's, its value having been originally pointed out by Professor Draper, of New York. The process is dependent on the fact that combination takes place between hydrogen and chlorine when the mixed gases are exposed to the action of light. The two gases may be evolved by the electrolysis of hydrochloric acid, and then they are in the right proportions for recombination. Such a mixture of gases, when exposed to sunlight, combines with explosive violence, though in diffused light the recombination takes place gradually, and in proportion to the intensity of the light, and to the time during which they are exposed to it. This affords a method of securing a registration of the intensity of the light, for the hydrochloric acid formed may be collected in water, and the amount may be estimated by various chemical means. For general use this method did not prove altogether satisfactory, and Bunsen and Roscoe abandoned it for one which will be described in detail. Professor Draper

had also pointed out that ferric oxalate when exposed to light gives out carbonic acid, and in 1859 Mr. H. Draper, of Dublin, turned this fact to practical use by elaborating a system of which the following is an outline.

The chemical reaction on which the method is founded is this :



$$\text{Ferric Oxalate} = \text{Ferrous Oxalate} + \text{Carbonic Anhydride}$$
$$Fe_2 3C_2O_4 = 2FeC_2O_4 + 2CO_2$$

The light vibrations are able to split up the ferric oxalate molecules, and for each molecule so shaken, one molecule of carbonic anhydride is liberated. Mr. H. Draper's apparatus consisted of 500 grains of a standard solution of ferric oxalate held in a glass cistern, rendered opaque by japanning, the light being admitted by leaving uncovered one square inch of the cistern. After exposure to the light for any desired time the amount of carbonic anhydride disengaged was known by the difference in weight before and after exposure, the loss due to evaporation being checked by comparison with a similar cistern containing distilled water. There are one or two objections to be noted as regards the accuracy of this method. The ferric oxalate being a coloured solution, it is uncertain to what depth the light penetrates into it, and it has yet to be proved that with equal intensities of light acting for the same time through the *same* aperture, double the same amount of chemical decomposition is produced after passing through two units of thickness, as is produced after passing through one. In all apparatus of this kind, too, the surface reflection has to be taken into consideration, as also the material of which the transparent parts of the cistern are constructed. If we could be assured that the value of the ultra-violet rays increased in the same ratio as the blue rays, the apparatus would suffice, but we have reason to think that this is not the case. Hence this construction must be taken as yielding an approximation to the true results rather than as the

true results themselves. We consider that the best results would probably be attained by throwing certain definite portions of the spectrum on some medium, and noticing the results of each. This would give a true idea of the relative amounts of photographic energy existing in each portion. It cannot be too deeply impressed on the student that these processes do not measure the *actual* energy in the impinging rays of light; this is altogether a different matter, into which we cannot enter here.

Professors Bunsen and Roscoe conceived the first practicable method of measuring the actinism of daylight and sunlight, by the exposure of sensitive silver chloride paper to their action for certain lengths of time. After an elaborate investigation, they came to the conclusion 'that equal quantities of the intensity of light into the time of insolation (exposure) correspond, within very wide limits, to equal shades of darkness produced on chloride of silver paper of uniform sensitiveness.' Starting with this idea they carried out a laborious research into the preparation of a paper that should be uniformly sensitive, and which might, therefore, be considered as a paper of standard sensitiveness. The following is a short *résumé* of their work: Choosing sodium chloride as the soluble chloride, they found, 1st, that a paper will not give uniform results when simply floated on the solution; but that it must be immersed in it. 2nd. That the stronger the solution the greater sensitiveness would be given to the paper. It was therefore necessary to fix some reasonable limit to the strength, and this they fixed at a 3 per cent. solution. 3rd, that using the sensitising solution of silver nitrate above a greater strength than 6 per cent. gave no difference in the results as regards sensitiveness, but that below that strength it rapidly diminished. 4th. That the presence of the salt resulting from the decomposition of the sodium chloride and silver nitrate had no effect on the sensitiveness, and that at ordinary temperature and moisture the sensitised

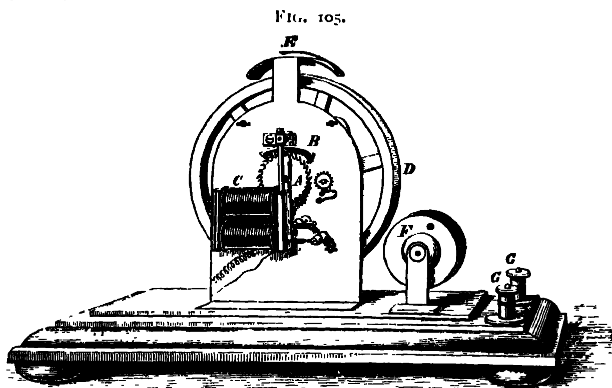
paper would keep at least fifteen hours unaltered. 5th. That the thickness of the paper employed had no material influence on the result—an important point, as in comparing the darkening due to the light with a standard scale of graduated tints it was necessary that the paper should be sufficiently opaque to cut off all shade from the tint beneath, which might shine through the paper. 6th. It was found that it was possible to impregnate 5 square metres of paper in a solution containing 60 grammes of sodium chloride without any danger of reducing the strength of the solution to such a degree as to cause any variation in sensitiveness. 7th. The time of sensitising, between fifteen seconds to eight minutes, also caused no alteration in the readings.

It will be noticed that the above results give great latitude in preparing a paper, the only conditions absolutely necessary being that the paper shall be uniformly soaked with a 3 per cent. solution, that the sensitising bath of silver nitrate shall not be suffered to drop below a 6 per cent. solution, and that the sensitising shall not be less than fifteen seconds of time. With such a preparation we have then a standard paper which will give uniform results—that is, we have a paper which, when exposed for a certain time to a certain intensity and *quality* of light, will always produce the same amount of darkening. The most perfect method of measuring intensity of daylight, then, would be to cause a strip of sensitive paper to pass gradually before an opening of a certain size, such opening to be exposed to the zenith. Unfortunately, this method is impracticable; for, as we shall find shortly, the darkening action in strong light, such as we have in sunshine when the sun is in the meridian, is exceedingly rapid; whilst in weak light such as we have on a cloudy day, the darkening is exceedingly slow. It might be suggested that the opening should be wedge-shaped, so that the shade itself might be graduated and therefore be readable at some part, and at a very early date in the history of photography this plan was proposed by

Mr. Jordan; but practically it is found that the opening necessary for the production of a readable tint in full sunshine, with paper passing slowly before it, is so small that there are mechanical difficulties in the way of securing accuracy; and when it is considered that one end of the aperture would have to be at least 100 times the width of the other, the impossibility of obtaining a proper gradation with a slip of paper of reasonable width is apparent. To meet this difficulty a most ingenious instrument was devised by Professor Roscoe, in which exposure takes place for certain regulated times, at fixed intervals, during every hour.

The registration is effected by the following contrivance (fig. 105):

Fig. 105.



A long strip of paper is rolled upon F, and fastened to D. In the latter is a clockwork arrangement, the escapement, B, being placed as shown. To move the clockwork, the armature of an electro-magnet C takes the place of a pendulum, and every time it is attracted and released by the magnet, a tooth of the wheel A is released, and the paper is moved a small piece forward across the weak spring, E, which is seen on the top of D. The use of the spring is to cause the paper to be in contact with a circular aperture of about

$\frac{1}{4}$ inch in diameter, left in the cover of the instrument, and through which the exposure is given. The result of the exposure is thus to leave circles of more or less blackness (the blackness varying according to the intensity of the light and the time of exposure) at intervals along the strip of paper.

The different exposures were given by a toothed wheel annexed to a clock, which gave the necessary contacts for fixed times to move the armature in fig. 105.

This instrument has been superseded by a form in which the paper is sensitised in a sheet and wrapped round a cylinder attached to clockwork. The cylinder moves round at intervals every hour by the clockwork, and when a complete revolution has taken place it shifts laterally, so that a fresh piece of cylinder is brought under the aperture.

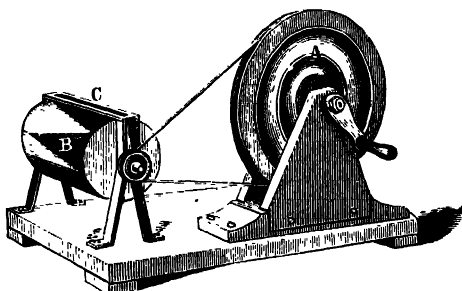
The following is the standard tint of grey adopted by Roscoe. He took 1,000 parts of zinc oxide and 1 part of lamp-black, and ground them thoroughly together to such a point that no further grinding altered the tint. This he found the most convenient tint for comparison; and, when carefully gummed on to paper, it was unaltered in shade. This mixture then gave the shade from which all his measurements were made, all other tints being referred to it.

To obtain a graduated shade he applied what is known as the pendulum apparatus, which in general outline consists of a pendulum swinging in front of sensitised paper in such a manner as to give a gradation of exposure to it, and a consequent variation in tint. At each point of the paper the time of exposure was known, and the point was then found answering to the standard tint, and the relative values of the other portions of the gradations calculated.

It may perhaps be found necessary hereafter to apply a correction to those readings taken in sunlight, as it may be found that the different integrations of the spectra formed by sky, cloud, and sunlight produce slightly different effects.

Another method of securing uniformity in measurement has been employed by the writer. It consists of a rapidly revolving cylinder, or drum, B, on which is attached a series of black and white sectors, as in the diagram. A convenient length for this drum has been found to be 6 inches. To the cylinder, B, is fixed a small pulley firmly attached to one end, over which is passed a cord communicating with the wheel, A. These are of such relative dimensions that the cylinder rotates at least fifteen times in a second, when A is caused to rotate but once. Along the top, and nearly touching the cylinder, is a blackened brass support, C, with a slot in it, on each side of which is a scale of inches,

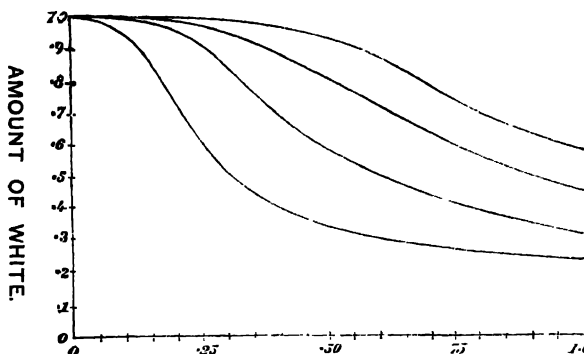
FIG. 106.



dividing the length of 6 inches into 120 parts, that is, each inch into 20 parts. Monochromatic light is thrown vertically downwards, on the scale, and any tint to be compared is brought on to the scale, and moved till an exactly identical shade is found on the rotating cylinder. A series of six readings is taken, beginning by moving the tint from white to black, and next from black to white. It will nearly always be found that this is necessary, as the readings in one case would be as much too high as in the other they would be too low. A mean of the six gives very nearly the truth. The accompanying diagram (fig. 107) gives the results of the reading of a strip of paper which had been exposed beneath

an apparatus, giving an arithmetical progression of exposure for each unit of length :

Fig. 107.

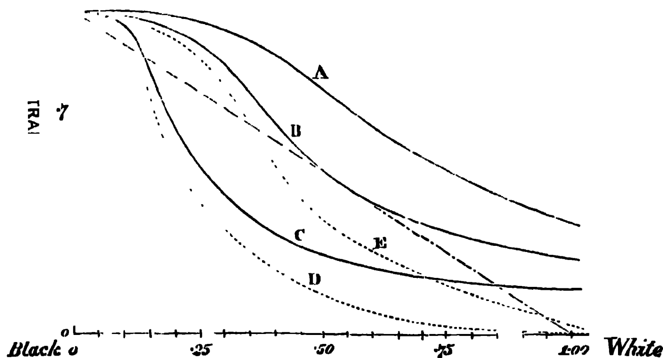


The ordinates measure the amount of white, 1·0 being white, and o black. The abscissæ show the exposure, with a fixed intensity of light. From a curve of this kind, when the tint is compared and known, and the time of exposure is also known, the intensity of the actinism can be judged. Roscoe's standard unit has an ordinate of ·76, that is, it is a visual combination of 24 parts of black with 76 of white.

This method of examining the gradations caused by different intensities is well worthy of more complete study, as it throws much light on the false effects which are produced in photographs. If we prepare a rotating wheel with black spokes so cut that when rotating in front of a uniformly lighted surface they give the exposure along the length of the spokes in arithmetical progression (thus : if the length of spoke be 10 inches, the exposure at that distance is 1, at 5 inches $\frac{1}{2}$, at $2\frac{1}{2}$ inches $\frac{1}{4}$, and so on), we shall find, on exposing a plate to the image of this rotating wheel as formed by a lens, or by causing the wheel to pass close to it, that the gradation of the negative obtained, when viewed by transmitted light, will not coincide for any length with

the gradation as seen by the eye. The following figure (fig. 108) shows the results of measurements obtained by the diaphanometer,[1] from plates to which different exposures have been given behind the rotating wheel. A, B, and C are the curves from ordinary wet-plate negatives. The ordinates measure the amount of transparency, 1 being total transparency, and 0 total opacity; the abscissæ denote the relative times of exposure, or what is approximately equivalent to it, the relative intensities of light acting on the negative, supposing Roscoe's law referred to above to hold good. It

FIG. 108.



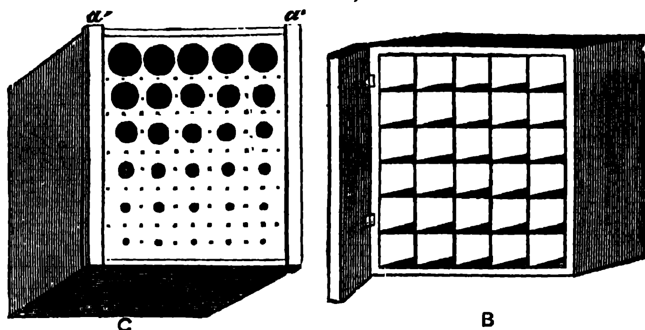
will be seen that the curves have very nearly, that is, within the limits of error of observation, the same form. Thus, taking the exposure of A equal to ·5 and 1, or 1 to 2, the corresponding transparencies are ·77 and ·37. Taking the same transparencies of B, the times of exposure are ·34 to ·66, or very nearly 1 to 2. The same will be found with C; the dotted curves, E and D, show a portion of the negatives, B and C, intensified in the ordinary manner, and the same relation to exposure still holds good. This is an important point, as it shows that the same relative intensities of light

[1] See *London, Edinburgh, and Dublin Phil. Mag.* Sept. 1874.

are maintained in a negative as the opacity is increased. The ordinates to the chain-dotted straight lines show the transparency that should result if photography gave perfect gradations. It will be seen that the tendency in all negatives is to cause a loss of gradation in the deep shadows as well as in the lights. This accounts for the loss of detail that is always seen in the extreme tints of a photograph. It is also worthy of remark that a thin negative seems to give a better gradation than one intensified.

It must be distinctly understood that the above curves apply to negatives only under one class of development. Under others the curves would show considerable variations. Amongst the most striking would be the form they take when near the parts in which total transparency is represented. A more detailed account of these will be found in the 'Photographic News' for July and August 1877.

FIG. 109.



An excellent instrument for making investigations on the density of deposit of negatives and for the darkening of different papers is what is known as Spurge's Sensitometer.

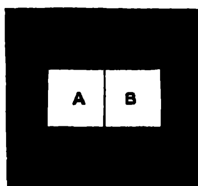
In fig. 109 C represents the appearance of the top and B that of the bottom of the instrument. Each of the various holes shown in C has a fixed ratio of 1 to $2^{\frac{1}{2}}$ with the

next hole. Thus the amount of light admitted to the plate or paper is halved every third hole.

By employing such an instrument almost every variation in the action of light may be studied.

A simple method of measuring densities of a negative has been devised by the author. A square hole is cut in a thin plate, rather less than the size of the square of density to be measured. Over the front of this hole is pasted white paper, by preference medium Saxe paper, and in a mask of black paper is cut an oblong twice the length of the square hole and of the same height. It presents the appearance from the front as shown in fig. 110. A is the paper with the square hole behind it, and B a white opaque square. If a small argand lamp be placed behind A it will become illuminated, and the surface B may be illuminated by a similar lamp from the front, if a rod be placed so that its shadow falls exactly over A. The two spaces can be made equally bright if the rotating sectors be placed between the front light and B. These sectors are attached to a small electro-motor which works with four Grove's cells. The aperture of the sectors can be increased or diminished during motion by a simple arrangement. This is an admirable plan of graduating light, and answers for all purposes of the sort. If a portion of a negative be placed almost touching A the light on A will be dimmed, and the sectors will have to be closed for equality of light to be again established. The ratio of the apertures of the sectors in the two cases will give the amount of light transmitted through the negative. This plan was adopted because it was found that the apparent density of a negative varies according to the distance it is from the receiving source, it being optically denser when far away from it than when close. This is due to a scattering effect of the small

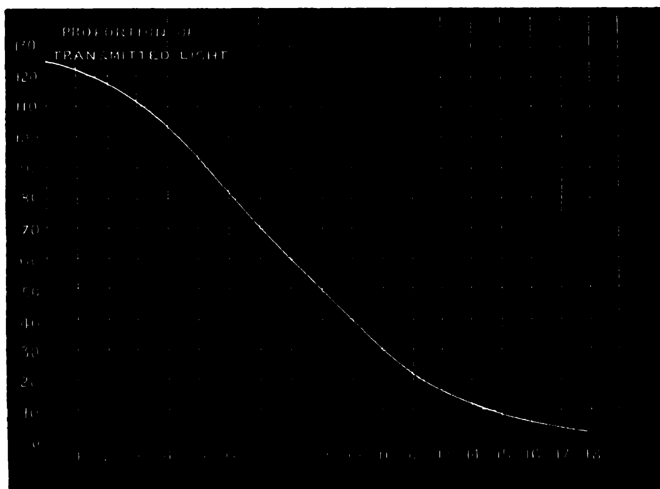
FIG. 110.



particles which make up the density of the negative. By placing the negative almost in contact with the receiving source this difficulty is avoided, and gives an accurate measure of the printing density of a negative, provided, of course, the negative has a black deposit.

The following figure and table give an idea of the value of a gelatine plate exposed behind Spurge's sensitometer and developed with ferrous oxalate and measured in this instrument.

FIG. 111.



The figures at foot correspond with number of hole in sensitomete

	Angular Aperture.		Angular Aperture.
Naked light	177	No. 9 square	$51\frac{1}{4}$
Glass and gelatine film .	$124\frac{1}{2}$	,, 10 ,, ...	$40\frac{1}{4}$
No. 1 square	$121\frac{1}{2}$	,, 11 ,, ...	$29\frac{3}{4}$
,, 2 ,, ...	117	,, 12 ,, ...	$21\frac{1}{2}$
,, 3 ,, ...	111	,, 13 ,, ...	17
,, 4 ,, ...	105	,, 14 ,, ...	12
,, 5 ,, ...	96	,, 15 ,, ...	$10\frac{1}{2}$
,, 6 ,, ...	83	,, 16 ,, ...	$7\frac{1}{2}$
,, 7 ,, ...	$71\frac{1}{2}$	,, 17 ,, ...	$5\frac{1}{2}$
,, 8 ,, ...	$60\frac{1}{2}$	,, 18 ,, ...	4

Putting this table another way, it means that the light in passing through the various parts is diminished by so many 177ths, thus—

No. 1 square allows $\frac{105}{177}$ of the total light to pass ;

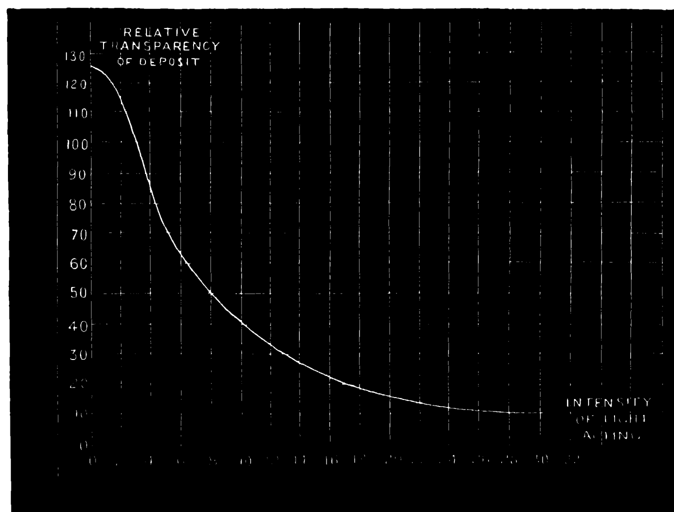
No. „ „ $\frac{96}{177}$ „ „

The film and glass $\frac{124\frac{1}{2}}{177}$, or ·7 of the light nearly ;

and so on through the whole scale.

The following figure shows the curve of density of the same negative for intensity of light increasing in arithmetical progression.

FIG. 112.

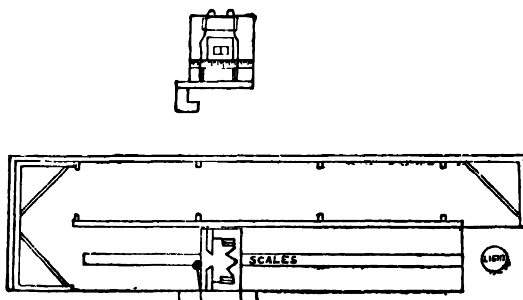


Sometimes it is convenient to form a screen of varying thickness, such as Warnerke's, and this may be done by taking a uniformly coated plate and exposing adjacent portions of it through a square aperture to a feeble light,

say of a 10-candle gas flame 10 feet off, commencing with 10 seconds' exposure, and going up next to 12½, then to 16, next to 20, next to 25, next to 32, then to 40, and so on, doubling the exposure every third hole. The development should take place with ferrous oxalate carefully neutralised, to which are added two or three drops per ounce of a 4 per cent. solution of potassium bromide. The development should be carried sufficiently far to render the most exposed square nearly opaque, and then it should be optically measured as described above. It has been found that the deposit given by ferrous-oxalate development is practically black, and that it cuts off the visual and the photographic rays in approximately the same proportion.

Such an instrument is excessively handy when Spurge's sensitometer is absent, and the results can be equally relied upon.

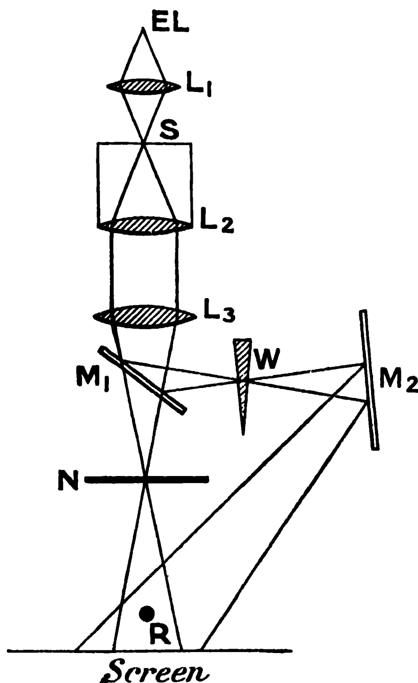
FIG. 113.



Mr. Chapman Jones has introduced a useful modification of the foregoing, using only one light for the purpose of measuring. He employs a screen, as shown at fig. 110. This is placed on a carriage running on a scale as shown in fig. 113. The light shines directly upon one side of the Abney screen, and by means of three mirrors and a velvet-lined tube with diaphragms, as shown, a beam is brought

round to the other side of the screen. There is a rod to cut off the light from B. The screen is moved till the transmitted and reflected beams appear of the same brightness, and the point on the scale where this occurs is the zero point. The density to be measured is then placed in position.

FIG. 114

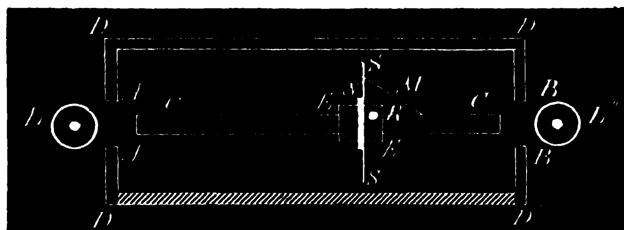


For measuring small sections of negatives, such as the negatives of the spectrum, the following plan is adopted by the writer. E L (fig. 114) is an electric light; an image of the carbon from it is thrown by a lens, L_1, on to S, a sector. L_2 is a lens placed at its focal length from S, so that the

rays run parallel and fall on L_3, a lens which forms an image of the sector S on N, the negative, narrow portions of which have to be measured. M_1 is a plain piece of glass which reflects a percentage of light on to M_2, a silvered mirror, and which then falls on the same screen as the direct rays. A rod, R, casts two shadows side by side. A black glass wedge, W, or rotating sectors are placed in the path of the beam, the apertures of which can be altered at pleasure, and the two shadows are made equally bright. The negative is moved along the image of the slit as required, and so transparency measurements can be made.

The apparatus the writer now uses (fig. 115) is a modification of Mr. Chapman Jones's instrument, but simpler in

FIG. 115.



some respects, though two lights are employed. D D D′ D′ is a box 2 feet 6 inches long by 9 inches broad and high. D′ D′ is a side of the box left open, but which can be covered by a black cloth. A A is an aperture sufficiently large to allow the whole of the light from the lamp, L, to illuminate the covered aperture in the screen, S S (fig. 115). B B is another similar aperture for the light of L″ to traverse. Behind S S, the negative N can be placed over the aperture in the screen. The rod, R, casts a shadow over the paper covering this aperture. M is a silvered mirror in which the double squares can be viewed. E E is a cradle carrying

S S, R, and M, which can move along on a batten, C C. A scale is placed along D′ D′, so that the distance of the screen from each light can be read off.

This scale is conveniently made a logarithmic scale, as first carried out by Messrs. Hurter and Driffield in their measuring box, since it enables the squares of the distances from each light to be readily found by logarithm tables. If this scale or an ordinary scale be used, it is convenient that the zero point should either be exactly half-way between the lights or else start exactly opposite the centre of the light directly illuminating the white square—in this case L″. The two squares can be made to appear equally illuminated by moving the screen, S S, and the distances (or logarithms of the distances) noted, and then the part of the plate whose transparency is to be measured is placed with a clip over the aperture in the screen, and equality of illumination again arrived at by a further movement of the screen, S S. The distances are again noted, and from these measures the light transmitted through the negative is readily calculated.

The author, in a paper communicated to the Camera Club in 1888, showed that the density very nearly approached the $\log^2$ of the time of exposure, or of the intensity of the light acting to form the image when a constant depending on the rapidity of the plate was added to it. This subject he subsequently expanded in 1893.

If E be the exposure (*i.e.* intensity of light × time), C a constant, then the transparency T of a developed negative may be represented by

$$T = \epsilon^{-\mu (\log E + C)^2}$$

C is a measure of the rapidity of the plate, and the rapidity of two plates can be compared by finding the value of C in the two cases.

Where the abscissæ to the curve are plotted as logarithms it assumes the same form as the curve given by the law of error, and it has a singular point through which a tangent

can be drawn, which lies closely along the curve, and always cuts the axis of y at a point which has a value of $2\epsilon^{-\frac{1}{2}}$. Taking the maximum transparency as unity, it has a value of 1·212; the singular point itself also has a value of T=·606.

Hence C can be found graphically very readily, and any calculation avoided. All that is necessary is to measure three or four densities close to ·606, plot the abscissæ as logarithms, draw a line through these points, and note where it cuts the line drawn 1·212 above the axis of x.

This will give the value of y where x=0.

If we measure the zero point from the same exposure in two plates, the difference between the two will give, in terms of log², the difference of the rapidities, and can be at once found.

Messrs. Hurter and Driffield in 1889 brought out another formula, which is based on scientific considerations. This when reduced to the simplest case gives very approximately good results. They find that

$$T = \gamma\epsilon^{-(\log E - c)},$$

or, as they express it, where D equals $\log \frac{1}{T}$,

$$D = \gamma \log \frac{E}{i},$$

i being the inertia (as they express it) of the plate. Their more elaborate formula runs as follows :

$$D = \gamma \log \left(O-(O-1)\ \beta^{\frac{E}{i}}\right),$$

where O is the opacity of the unexposed plate, and $\log \beta = \frac{1}{O}$.

In determining the speed of a plate Messrs. Hurter and Driffield [1] allow the light of a standard candle to fall upon

[1] The original paper was printed in the *Journal of the Society of Chemical Industry*, and was supplemented by other papers, notably an address to the Photographic Section of the Liverpool Society on January 19, 1891, and a paper on 'Latitude in Exposure and Speed

a strip of the plate placed at a distance of one metre, and adopt the term 'candle-metre second' as the unit of measurement. (It may be noted that the unit of light is somewhat uncertain.) Between the candle and the plate, and immediately in front of the latter, they place a revolving disc having an opening in the form of nine steps, each of which permits twice the amount of light to pass which is passed by the preceding step, the amount of light passed being in geometrical progression. These nine exposures occupy nine-tenths of the length of the strip; the remaining tenth of the plate is shielded from light and is described as the 'fog strip.' In testing an unknown plate they recommend that the exposures should range from 80 c.m.s. down to 0·312 c.m.s., and that development should be by ferrous oxalate (see p. 169), to be continued for from five to six minutes. The completed strip is measured in the apparatus, fig. 116. Measured apertures are provided at each end of the box which the light from the flames of two lamps will completely fill, the lamps being close to the apertures. At one end the negative to be measured is placed, and at the other is a graduated diaphragm to cut off more or less light, as may be desired. The cubical box shown in the centre is fitted with an eyepiece: it contains a Bunsen screen, and can be caused to slide from one end of the chamber to the other. The alteration in the illumination of the two sides of the screen is effected by moving it. The opacities of the negative are read off on a scale in front (to avoid calculations they are given in logarithms of the opacities, which are called the densities). These densities are marked upon skeleton diagrams, the density of the 'fog strip' being first deducted from the densities of the exposed portions. The abscissæ are the exposures in powers of 2. The points so obtained furnish a curve of double flexure, and show what the authors call under, correct, and over

of Plates,' read at the Photographic Convention, July 1893. These papers were printed in the photographic journals.

FIG. 116.

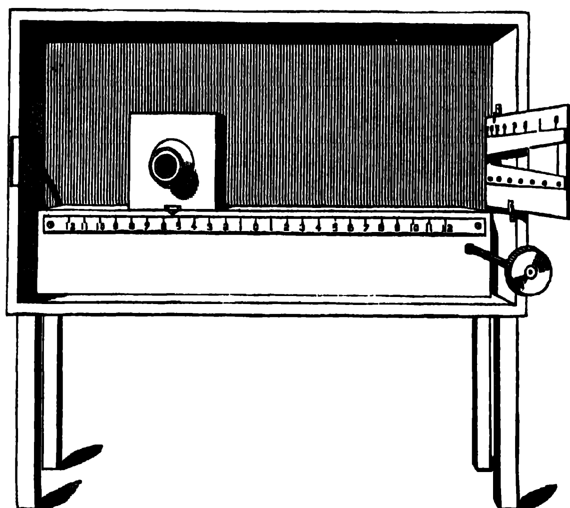
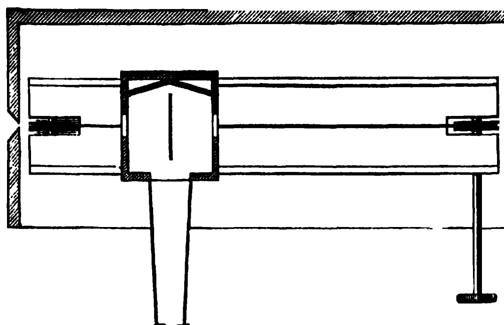


FIG. 2.



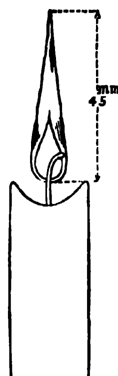


FIG. 3. SLIDING SCALE.



exposure. The straight part of the curve is continued down till it intersects the scale called the inertia scale at the bottom of the diagram, the inertia scale being the exposure in candle-metre seconds. The point at which the intersection takes place gives the 'inertia' of the plate, which is then converted into the 'speed' by dividing it into the constant 34.

The straight line is said to represent the period of correct exposure, the curve above the straight line is said to represent the period of over-exposure, whilst the curve near the base is said to represent the period of under-exposure. Prolonged development will raise the curve high on the diagram, and brief development will lower it; but whatever the development may be, given the same exposures upon the same plate, the straight line should always intersect the inertia scale at the same point.

If a line be drawn parallel to the straight line connecting the curves from point 100 on the inertia scale, the point where it intersects the right-hand vertical scale gives what is called the development factor.

For the purpose of speed determination it is best that a development factor of 1·0 or a little more should be attained.

Details of Hurter and Driffield's method of the determination of the speed of a plate are given somewhat fully, as, at the present time, many plates are on the market whose speeds are given on this scale. The method is open to criticism on several grounds if carried out as recommended by them. In the first place, the exposures by apertures in a rotating disc are apt to give false densities, as already indicated. This can be avoided by giving time exposures by hand, the light remaining in a fixed position. What that position should be is doubtful, since the apparent exposure diminishes in effect as the light is farther from the plate, and in the case of slow plates the difference is very marked. Hence a plate may have any number of speeds, according to the light in which it is to be used. For quick

plates the difference may not be practically appreciable (see p. 399). The method of measurement advocated is also subject to a defect which, whilst it may not affect the speed determination, yet fails to give the true density as used in printing. The light passing through a negative is scattered to a certain extent by the granular deposit, very much as ground-glass scatters it. Approximately, if the densities (*i.e.* the log. of opacities) are multiplied by ·7 the true printing densities are arrived at. The writer is also averse to the concave part of the curve being called the period of under-exposure, that being the portion which in a photograph has to render the shades between the half-tones and the deep shadows. In fact, it is a most useful part of the exposure. In an instance where two curves have been plotted the transparencies of one negative range from total transparency to a reduction of 31 per cent. of the light, and in the other from total transparency to 25 per cent. of the light. If a plate could be made in which the inertia was 0, then the curve would be a straight line till the period of so-called over-exposure was reached. The contention of correct exposure can only be held to be exact when the deepest shadows of a view on a plate of which the first curve gives the speed are represented by a density of ·5, the other densities being in like manner increased. Such an increase in exposure would be intolerable, and the speed of the plate on these lines would be very considerably less than that supposed to exist; in fact, no photographer would tolerate such a speed. In order to take into account this concave part of the curve the writer proposed the plan already described, in which the *transparency* of deposit is measured, and not the density.

Exposure Meter

Mr. Alfred Watkins has placed upon the market an ingenious instrument which he calls an exposure meter,

and no doubt it has proved useful to many in enabling them to judge of their exposures. It is, in fact, a calculating machine for putting together all the factors which have to be considered in exposing a plate. The value of the light is claimed to be known by exposing sensitive paper with its face in the same direction as the light falling upon the subject. This we hold to be a mistake, as all exposures should be made for the shadows, and it is the sky which illuminates these if they are open ; and in using it, the writer has found that it is better to point it towards the part of the sky at right angles to the direction of the sunlight, if there be any. The value of the sunlight should scarcely be considered, which would not be the case in a landscape if the directions were carried out. As full directions are given with each instrument we need not deal with it in fuller detail.

CHAPTER XXXVII

TRUE MONOCHROMATIC RENDERING OF COLOUR

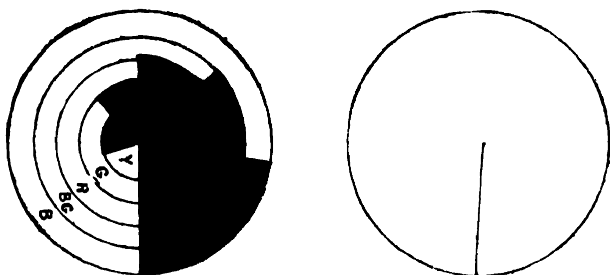
A REFERENCE has been made in chap. xxxv to the use of yellow glass in front of the lens for rendering colour more perfectly in monochrome than is the case when ordinary white light reflected from the objects is admitted through the lens ; but unless this yellow glass be of a particular tint—which tint must vary for every kind of plate employed—the monochromatic rendering of the colour will only be approximately true. The writer has prepared a sensitometer which will indicate how closely the true effect can be obtained by gradually altering the hue of the medium through which the light passes to the plate. Glasses which transmit white, red (glass 'stained' with orange on one surface and with ruby on the other), yellow, light bottle green, peacock blue, and blue (cobalt blue)

are cut into small squares of half-inch side, and are cemented in a row on to a flat piece of white glass. The intervals between the glasses and the space surrounding them are covered with a black mask, so that the only light passing through is that coming through the glasses. The luminosity of the light passing through each specimen of glass is measured by the plan given in 'Colour Measurement and Mixture.'[1] We will suppose that the following are the luminosities: White, 100; red, 30; yellow, 80; bottle green, 40; peacock blue, 25; cobalt blue, 20. A disc is cut out as shown below, which is rotated in *front* of and close to the row of coloured glasses; the cobalt is left bare, the peacock blue has an opening of 288°, the remainder of the annulus being opaque, for 288° is $\frac{20}{25}$ of 360°, the bottle green has an opening of 180°, the yellow of 90°, the red of 240°, and the white of 72° for similar reasons. The glasses, if viewed against a white light when the disc is rotating in front of the glasses, will appear of equal luminosity. If a sensitive plate be placed behind the sensitometer the deposits on the negative, which are caused by the light coming through the glasses, will be of varying depths, though for perfect monochromatic rendering of the colours they should be the same. By admitting light to the sensitometer through different media the requisite equality can be arrived at by a trial, always supposing the plate itself is in some small degree sensitive to the orange of the spectrum, a colour which is also to be found in the light coming through the red glass. Supposing after a trial it is found that the green is much too feeble, then evidently a medium through which to admit the light allowing more green to pass must be found. By this system of trial a screen to be used in front of the lens can be worked out. A plan, which is also simple and equally effective, can be found by the use of pigments. Paint a cardboard disc of 4 inches diameter with chrome yellow, and place it on a

[1] S.P.C.K. 'Romance of Science' series, by the author.

rotating apparatus with black-and-white discs of 8 inches diameter interlocked behind it (see fig. 117) and cause the three discs to rotate together. By altering the proportion of black to white in the larger discs the luminosity of the grey can be caused to match that of the yellow, and it becomes an easy matter to make a very exact match by observing the rotating discs through a black medium (such as that given by a deposit on a negative when developed by a metol developer), when the colour of the yellow will become quite unobtrusive. Suppose to give this equality the proportion of black to white is 50° to 320°, and that the black reflects 4 per cent. of white light, the luminosity of the yellow will be nearly

Fig. 117.



$\frac{322}{360}$ of the white; and if we call white 100, then that of the yellow is 89·4. In a similar way the luminosity of emerald green may be ascertained. In the case of the yellow and the emerald green investigation has shown that their luminosities and that of white diminish proportionately as the white light in which they are viewed is diminished. Having ascertained these two luminosities, that of any other pigment may be ascertained. Discs of 4-inch diameter of the yellow and green, and also of French blue toned lighter with a little flake white for convenience sake, are interlaced and placed on a spindle with the discs of white and black also interlaced behind them. The five discs are rotated together, and by alteration of the proportions of the three

colours a grey is obtained which can be matched with that of the black and white. The angles occupied by the various sectors are measured, and by a simple calculation the luminosity of the blue can be ascertained. The yellow is replaced by a disc of red, and the same operation is gone through, and, knowing the luminosities of the green and blue, that of the red can be calculated. The four colours with white are sufficient for the purpose in view. A white disc of some 8 inches diameter is divided into five rings of white, red, yellow, green, and blue, the last named by preference being nearest the centre, as it is the least luminous. The proper proportions of the coloured rings are covered up with black (the amount of white light reflected from the black being allowed for) to reduce them all to the luminosity of the blue. A camera can be employed to photograph this rotating disc, and the medium in front of the lens is changed till the deposit due to each ring is the same (see fig. 119). That the densities are equal can be seen by simple inspection, or a print in platinum can be made and cut in two portions, when it will be seen if the grey of each ring matches exactly. This last plan of experiment is a very useful one, as it enables the experimenter to use daylight for his trials, but it must be recollected that the results will only be true when the light in which the photograph is taken is the same as that in which the luminosity is measured. It will not do, for instance, to take the luminosity of the pigments or glasses in lamplight and photograph in daylight. It is true that daylight varies in quality to a certain extent, but for three or four hours on each side of noon a north light will give almost identical results in measuring the luminosities, and hence may be used for photography. Direct light from the sun varies considerably within these hours, and hence it should not be employed for illuminating such objects as coloured pictures which it is desired to render in true monochrome.

It must again be enforced that the screen which will be

correct for one class of plate will not be correct for another class. Thus the screen to use with a Cadett spectrum plate, in which the green is but little less photographically active than the parts of the spectrum on each side of it, will be totally different from that which is required for an Edwards' Isochromatic plate. It must be remarked here that it is almost impossible to render all the colours of the spectrum itself in correct luminosity. It is only because all objects in nature reflect a good deal of the spectrum, even when the colours are brilliant, that a correct result can be obtained in ordinary photography. The lack of sensitiveness in some parts of the spectrum is made up, as it were, by increased sensitiveness in others. So far this compromise is the only one which allows of approximate truth to be obtained. If a plate could be manufactured which would be equally sensitive to equal luminosities of all the spectrum colours, a really true solution of the problem would be obtained.

CHAPTER XXXVIII

TRICHROMATIC PHOTOGRAPHY

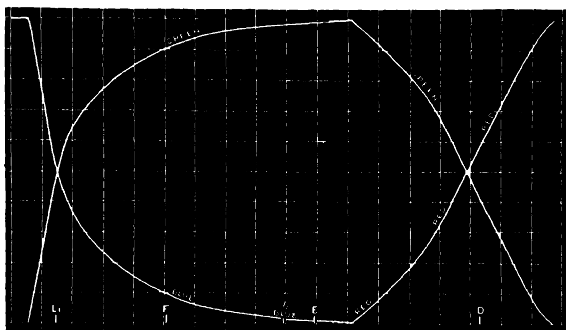
ANOTHER recent problem in photography has been the production of pictures in the colours of nature. There are two methods of producing the final picture. The one is by means of projection in a triple lantern or its equivalent, and the other by printing in transparent colours by carbon printing, or by ordinary colour printing.

It is not intended to describe the means of producing the picture, but only the negatives from which it is derived. The process is founded on the fact that a good red, a good green, and a good blue in the spectrum can as mixed light produce any colour in nature, including white. The

theoretical colours are those which are near the blue lithium, the red lithium, and the *b* lines of magnesium when these metals are vaporised in the electric arc. It is these colours which most effectually stimulate the three colour sensations in the retina in the greatest purity, and it is consequently these colours which should be the foundation on which the scientific photographer should work.

The first experiment, then, which has to be carried out is to match as closely as possible the rays of these parts of the spectrum with the light coming through transparent screens. In practice Mr. Ives, to whose researches the practical solution of three-colour photography is due, found that a signal green glass coated with a gelatine solution of a blue dye ('soluble blue' will answer) gave the screen which most nearly approached a match with the blue ray. The same glass backed by chromium green glass will give a good representation of the green, and a scarlet dye in gelatine will give a good representation of the red ray. These screens, it should be remarked, are those which should back the transparencies taken from proper negatives when the images from them are superposed. They are not the screens through which the negatives themselves must be taken. These have to be arrived at by a different plan. We must, however, suppose that we have started with screens such as are described above. We have to make a sensitometer by their aid which will give the screens required. Perhaps the most ready plan is to use pigments for the purpose somewhat in the way described in the last chapter. In the first place, we must choose our pigments well as before—a crimson red, a yellow chrome, emerald green, a French ultramarine blue, and white will answer our purpose. These are colours which are to be found in the spectrum, when a little white is added to them in some cases, as are also the colours of the screens. Fig. 118 gives the percentage of the three colours of the screens which go to make up all the colours of the spectrum, and we

can find the colours of the spectrum which match the pigments employed, and also the percentage of each colour in white light. We can then find the luminosity of each pigment as before in ordinary daylight if we wish. Let us take as an example of the next step the operations for finding the screen to produce the 'red' negative, and the red pigment to produce the chrome yellow. It is found, say, that 4 parts of red mixed with 3·5 parts of green will make the colour, and that its luminosity is 78 per cent. of the white light falling on it, while the red pigment requires to every 30 parts of red



Percentage composition of spectrum colours of equal luminosities (in terms of the red, green, and blue screens).

light 1 part of green light to match it, and that its luminosity is 18. It is evident that the yellow pigment must be reduced in luminosity to give a deposit of equal density with that of the red. Now only $\frac{4}{7\cdot5}$ part of luminosity of the yellow is due—the red light—that is to say, $\frac{4}{7\cdot5} \times 78$, or nearly 42 per cent. The luminosity of the red pigment is due to $\frac{30}{31}$ of the red light—that is, the luminosity of the red component is $\frac{30}{31} \times 18$, or 17·4. We must therefore reduce the luminosity of the yellow pigment so that the 'red' luminosity in both will be the same; that is, we

must reduce the 78 to $\frac{17\cdot4}{42}$ of its value—that is, to 32·3. The same procedure is adopted with the white. We can use any other colours in the same way.

Having calculated the luminosities, we then proceed to make a colour disc of rings (fig. 119) toned down by black to represent them. A screen must now be formed by trial which with a given kind of plate will give a developed image of equal density throughout (fig. 119).

To find the screen which is suitable for the 'green' negative, we proceed in exactly the same way, using the luminosity of the green light with which the pigment colours are made up, and calculating the reduction to be made in each one to bring such luminosity to an equality. A second disc is made as before, and we have then to find a screen which will make the photographed image appear of equal density throughout. We proceed in the same way to obtain the blue screen.

When the three taking screens are made they can be used to obtain the three negatives. Mr. Ives has introduced a special form of camera in which three images of the same object may be obtained by one exposure and on the same plate. The exposure given has to be that required for the screen which renders the light most photographically inactive, and this is done by means of an ingenious arrangement of stops and reflections of the image from plain mirrors. The three negatives may, however, be obtained in an ordinary camera by employing the three screens with three different suitable exposures.

A little thought will show that if a photographic plate could render gradations of light (of any colour) accurately, three perfect negatives would be obtained, and from them three perfect transparencies or prints would also result. As a matter of fact, the photographic gradations are not quite perfect, and therefore prints may be slightly wanting in absolute truth, though the colours of the print, or of the superposed images when a lantern is used to throw the

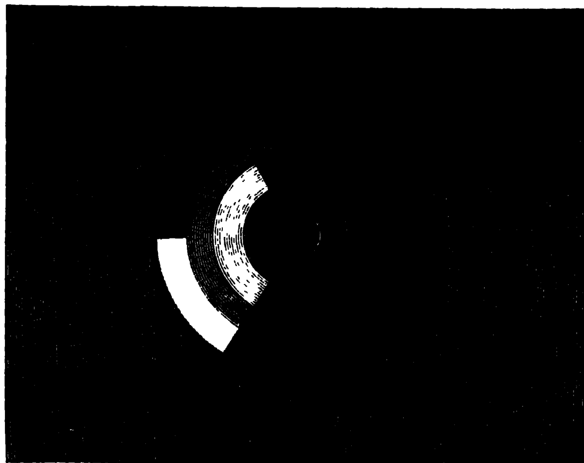
three images on a screen, with the red, green, and blue media behind them, will be true. A sensitometer made of

Fig. 119.





FIG. 119 (*continued*).



coloured glasses on the same principles as that described in the previous chapter may be substituted for the coloured discs.

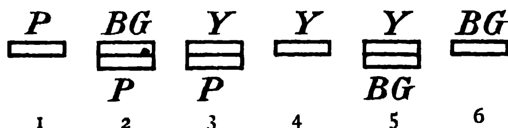
Regarding the production of prints by means of transparent films superposed or by means of transparent inks, it will be evident that the colours employed cannot be a red, a green, and a blue, but they must be approximately complementary colours. Red, green, and blue light, when mixed in proper proportions, will give a white ; but the light coming through red, green, and blue films, when superposed, will extinguish all light, or when pale will show a grey. The same thing will happen if the red and green are superposed, or the red and blue, or where pale a dark yellow or purple will be produced. If, however, we select a blue-green, a yellow, and a pink as colours to superpose, we shall find that we may get correct results. The blue-green dye or pigment allows the green and blue regions of the spectrum to pass, the yellow allows the red and green

regions as well as the yellow to be transmitted, whilst the pink will allow the red and blue regions of the spectrum to pass.

Suppose we have in an object a green patch, and take three negatives of it through the suitable screens. We shall find that in the 'green' negative the green patch is opaque, and in the other two negatives transparent. If we make gelatine transparencies by the dichromate process (see p. 229) from these three negatives, we shall have in the 'green' transparency the green patch shown as transparent, and in the other two the gelatine will remain intact. If we stain the red transparency with a bluish-green dye, the 'green' with a pink film, and the 'blue' with a yellow, and superpose these films, we shall have the full light coming through the blue-green and yellow films, and a green will be transmitted. In a similar way we can show that all other colours will be produced.

As it is not always possible to select dyes or transparent colours which will answer for printing the negatives taken for triple projection, a plan is here indicated by which the screens to be used in the production of the negatives suitable for the colours to be used may be made. Gelatine films are dyed, but not too deeply, with the colours to be used, and to such a depth that when superposed the light transmitted is a true grey and not showing any colour. From these films six coloured squares, say ½ inch wide, are prepared and placed between glasses. The squares are shown diagrammatically in section in fig. 120.

FIG. 120.



P is pink ; *BG* is bluish-green ; *Y* is yellow.
The colours are : 1, pink ; 2, blue ; 3, red ; 4, yellow ; 5, green ; 6, blue-green.

All these colours are not equally luminous by transmitted light, but they all are formed by what may be called the standard tints which make the grey as above.

For the three colours which contain a pink it is evident that in one of the three negatives the density of deposit must be as nearly as possible equal, and the other colours should impress themselves as little as possible. A screen, in this case green, is sought for by trial to do this.

Similarly with the three colours in which a yellow is used the same reasoning applies, and a blue screen of some kind must be obtained to give 3, 4, and 5 the same density, leaving 1, 2, and 6 to show little or no deposit. The screen, when the blue-green forms part of the colour, will be a reddish screen probably. The colours of the screens depend of course on the brand of plate to be used. When the screens have been found and the densities on the three negatives taken from the colours are equal, gelatine prints taken from them and dyed with the original dyes will reproduce the colours. It may be stated that absolute exactness cannot be got, but sufficient approximation can be obtained to make the process a success.

In some processes, when the printing is done by three typographical blocks, the choice of colours may have to be somewhat modified, for these blocks are usually prepared by the process which is given in chap. xxix., and consequently part of the colour is that which may come from only the printing of one negative, though the major part will be that due to the superposition of the three colours.

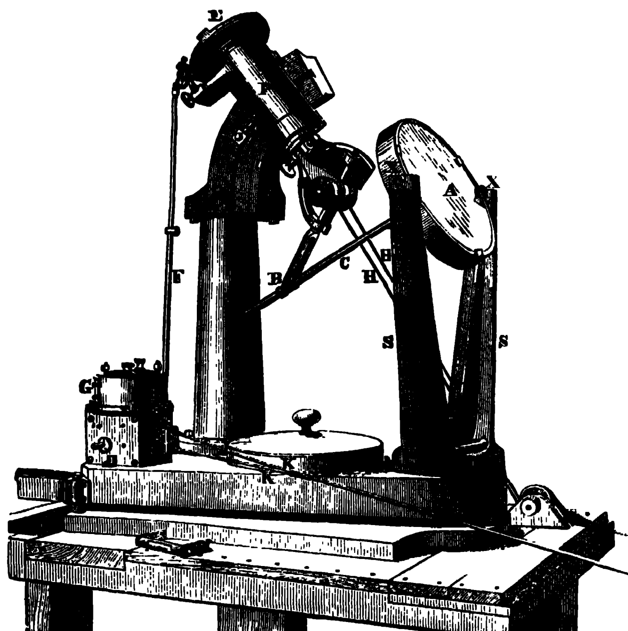
CHAPTER XXXIX

CELESTIAL PHOTOGRAPHY

Physicists have turned photography to account in their study of the heavenly bodies, most of which, in one way or another, have been made to impress their image on sensitive plates. The student who may take a landscape with the sun shining direct into the lens will soon satisfy himself that the exposure necessary to obtain a good photograph of our luminary, when unclouded, is very small, so short, indeed, that solarisation is frequently induced, though the landscape itself may be capable of proper development. Taken with the ordinary camera and lens a photograph of the sun is practically useless, since a lens of short focus is only capable of giving a very small image, and one on which none of the markings which characterise his surface can be seen, even with the aid of a magnifier. Since the prime object of solar photography is to enable the surface of the sun to be studied, it is evident that other means must be adopted in order that it may be delineated on a sufficiently large scale. A lens or object-glass gives an image of the sun of a diameter of about $\frac{1}{10}$ of an inch to each foot of its focal length. It is, therefore, evident that in order to secure a photograph of it of 4 inches (about 10 centimetres) diameter, the lens employed must have about 40 feet focal length. Now, 4 inches has been proved by experience to be about the least diameter for a solar image in which sunspots can be effectually studied. Before the introduction of Foucault's siderostat a telescope would have had to be mounted equatorially, and a clock motion would probably have been necessary, since the motion of the earth, even

with the short exposure necessary, would have marred the definition to a certain extent. Since siderostats have been classed amongst available instruments, the difficulty attendant on the mounting of such an enormous length of telescope has disappeared, and a lens of great length can be employed, mounted on a less heavy tube, placed in any convenient position, and supported in its length, if necessary,

Fig. 121.



along the ground. A siderostat belonging to the Royal Society, made by Cooke on Foucault's model, is given in the accompanying fig. 121. Its principle is the same as that of the heliostat, already described at p. 323, and shown at fig. 99. A is a mirror, silvered on the external surface, which has been worked to a perfect plane. It is suspended

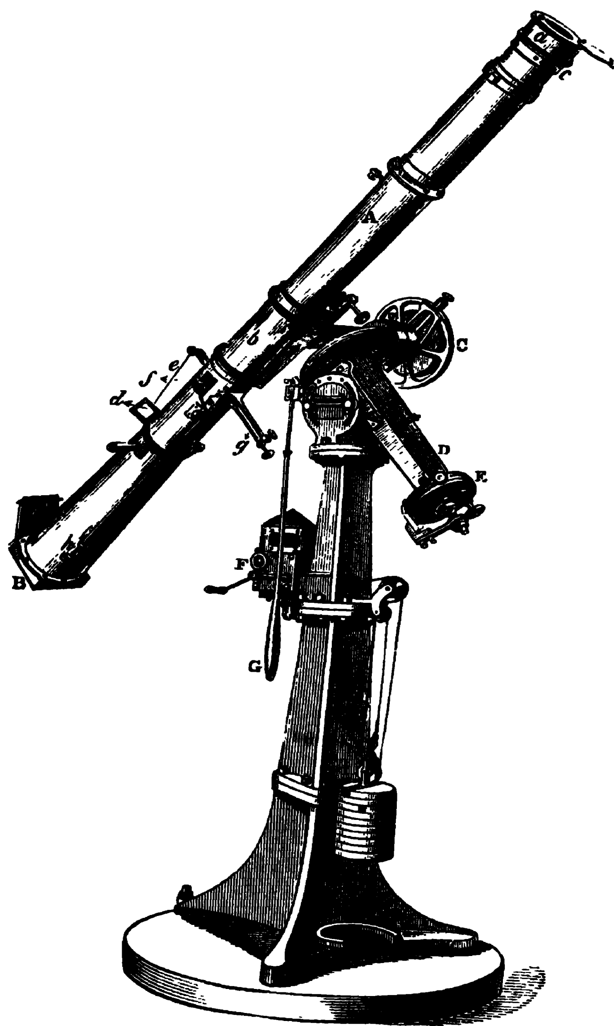
on two axes, X X, working a U-piece, S S, pivoted at the base, and therefore capable of moving the mirror so as to face any given direction. P is the polar axis, set so as to point to the pole of the heavens; the inclination being regulated by a movement along an arc, affixed to the principal supporting pillar of the instrument. Attached to the polar axis is the declination circle, E, to which the ordinary movement is given by the clockwork, G, which communicates its motion by the connecting rod, F. To the lower extremity of the polar axis is attached a movable arm, which can be clamped, so as to form any angle with it. At the bottom of this arm is a socket joint, pivoted at B, in which C, a rigid and perfectly true rod, is capable of sliding. When using the siderostat, it should be set with the polar axis in the meridian. The beam of light can then be caused to be projected in any given horizontal direction by the motion of S S, whilst its vertical direction is adjusted by the movement of the arm B. K K are cords which can turn F, and consequently E, and hence the motion of A in the horizontal plane can be adjusted without interfering with the movement of the clock. H H are cords working on the movable arm, to which B is attached; a vertical adjustment can therefore be given to the reflected beam.

The following method can be employed for obtaining a solar image with the lenses of very long focus by the aid of the siderostat. The lens with its tube is placed in a position such that the direction of their axes cuts approximately the centre of the mirror. Since the mirror is supposed to be a perfect plane, it is manifest that an image of the sun should be formed at the principal focus of the lens, as perfect as if the axis of the lens itself were pointed to the luminary. It is needless to describe the camera, which, in fact, instead of being attached to the tube, may remain detached so long as the plane of the sensitive plate is kept accurately perpendicular to the axis of the lens, and so long as all light, except that admitted through the lens, be excluded. This is,

perhaps, better than rigidly attaching it to the body of the tube, as it gives facilities for exposing the plate very close to the principal focus. It has been considered most important that such a position for the exposure should be obtained. The reason of this will be evident when it is remembered that the only means of giving the exposure is by causing an opaque screen, in which a slit is cut, to pass across the beam of light. Were such a screen passed in front of the lens, or at any part of the telescope other than the principal focus, the impression of the image might continue during the entire exposure. When the exposure, however, takes place at the principal focus of the lens, during each part of the exposure a definite portion of the image alone is impressed. To secure good detail in the representation of the sun's surface such a method of impressing the image is necessary, since, however excellent may be the workmanship of an instrument, there is always some small tremor in the movements, and consequently a risk of an imperfection in the image. There is much to be said in favour of this method of solar photography, and something to be said against it, and it seems a point which has yet to be decided as to whether this or the plan next to be described is likely to give the most accurate results.

A less unwieldy instrument which was first adopted for solar photography was one designed by De la Rue, and known as the Photoheliograph. The figure 122 shows the latest pattern, and is taken from one of those which were employed by the expeditions for observing the transit of Venus. At *a* is a lens of about 4 feet focus, having a cell on which is cut a very fine screw, so fine and accurate, indeed, that the lens can be caused to advance or recede from B by the $\frac{1}{1000}$th part of an inch by turning the cell through a portion of a turn. About *f* is the principal focus of the lens, at which point are placed cross-wires or a ruled grating; the focus of which can be accurately obtained by a slow-motion screw turned by the handle. This moves

Fig. 1



an inner tube in which the diaphragm holding the wires is inserted. Immediately in front of *f*, and running in a pair of grooves, is the exposing screen, in which there is an adjustable opening or slit. At *g* is a spiral spring, which tends to keep the slit below the point where the image is formed, whilst at *e* is a little pulley, over which runs a thread attached to the top of the exposing diaphragm, and terminating by a loop. The preliminaries to exposure are to draw the diaphragm up to *e* by the thread, and then to place the loop over a pin (not shown in the figure); this brings the slit *above* the place where the image is formed. The exposure is given by cutting the thread; the spring, *g*, pulls the diaphragm towards it, and the slit traverses the image. The duration of exposure can be regulated between $\frac{1}{20}$th and $\frac{1}{100}$th part of a second, a margin sufficiently wide to suit the sun as seen through almost any condition of the atmosphere.

Below *f* is placed a magnifying lens, which takes the form known as 'the rapid rectilinear.' Its function is the same as that of an eyepiece in a telescope, and by altering the distance between its optical centre and the focus of the object-glass any size of image can be produced. In the instrument under consideration the diameter of the sun's image has been fixed approximately at 4 inches, and consequently the adjustments of the secondary lens are made so that there cannot be much variation from those dimensions. B is the holder in which the slide carrying the sensitive plate is placed. Some of the means of adjustment have already been pointed out; a further one is that of the secondary magnifier, which by a slow-motion screw can be caused to recede or advance along the axis of the telescope. It will be seen that every means of securing a sharp image of the sun together with that of the cross-wires or ruled gratings is to be found in the instrument. The telescope is mounted equatorially, D being the polar axis, C and E the declination and right ascension circles, and F the clock movement. By means of G a motion can be given to the tube in right

ascension, and by a corresponding handle attached to the tube (and not shown in the figure) a motion in declination. The greatest danger to the accuracy of this instrument is distortion, through the multiplication of lenses, and the risk that exists of these not being properly centred. When attention has been paid to this, as it has been by the eminent optician who has constructed them, they leave little to be desired.

It is quite possible to get photographic images of the sun with an ordinary telescope, substituting a photographic lens for the eyepiece and fixing a camera behind to receive the image. A telescope of 5 feet focal length and a stereoscopic doublet will give a very fair image up to 4 or 5 inches in diameter. The main difficulty is in procuring a rapid exposing apparatus which, as has been said, should be at the focus of the telescope objective and should move without jar.

The best process for solar photography cannot as yet be said to be determined. Some observers state that the wet plate answers best, whilst others say that some one of the dry processes gives the finest results.

It seems that in the earliest days of the discovery of photography by Daguerre impressions of the solar image were made, and it would require a somewhat long list to record the names of those who have successfully adapted the art to astronomical purposes. For the registration of the phenomena connected with the total eclipses of the sun the same difficulties as to the names of the workers would arise. The first recorded endeavour to employ photography for this work dates back to 1851, when Berkowsky obtained a daguerreotype of the solar prominences during the total eclipse. From that date nearly every total solar eclipse, the observation of which was possible to European observers, has been studied by its aid, and has tended to the solution of some of the problems which arose concerning the solar physics. In 1860 the first regularly planned attack on the

problem by means of photography was made by De la Rue and Secchi, and in subsequent eclipses it has been continued.

As regards photographing the corona the general opinion seems to be that it is better to employ an ordinary photographic lens of a focal length of some 180 centimetres with the camera mounted equatorially, than to employ the ordinary telescopic objective. The coronal light during the eclipse is faint, and in order to get full effect it was necessary that the ratio of the aperture to the focal length should be as great as possible. Since the advent of the new sensitive processes it is now possible to use an enlarged image, such as given by the photoheliograph, though up to the present this instrument has not been employed with perfect success during eclipses. In the future, however, much may be hoped for by its employment.

Lunar photography has occupied the attention of various physicists from time to time, and, when Daguerre's process was first enunciated, Arago proposed that the lunar surface should be studied by means of the photographically produced images. In 1840 Dr. Draper succeeded in impressing a daguerreotype plate with a lunar image, by the aid of a 5-inch telescope. The earliest lunar photographs, however, shown in England were due to Professor Bond, of the United States. These he exhibited at the Great Exhibition of 1851. Dancer, the optician, of Manchester, was perhaps the first Englishman who secured lunar images, but they were of small size. After these might be mentioned many names, but it is unnecessary to refer to any before that of Crookes, who took the next step in the matter. The instrument that Crookes employed was an 8-inch refractor, belonging to the Liverpool Observatory, which had a focal length of about 12½ feet. The diameter of the moon was, therefore about 5 centimetres. Crookes affixed a small camera to the telescope and focussed the actinic rays by trial, there being found a great deviation between their focus

and that of the visual rays. The motion of the moon not being capable of being followed in the telescope by means of the ordinary equatorial arrangement driven by clock-work, the necessary accuracy was obtained by mechanically following it by means of the slow-motion screws attached to the declination and right ascension circles. The cross-wires in the finder were kept on one point of the image of the lunar surface, a highly magnifying power being used in the eyepiece. Crookes found that with different telescopes the necessary exposure varied between four seconds and six minutes.

In 1852 De la Rue began experimenting in lunar photography. He employed a reflector of some 10 feet focal length and about 13 inches diameter. An abstract of a paper read before the British Association appeared in the 'British Journal of Photography.' In it is given a very complete account of the methods he adopted.

In the first part of the paper De la Rue points out that if the image of a bright star is allowed to traverse a photographic plate, the result is not, as one would expect, a straight line, but one which is broken up and disturbed, and which consists of an immense number of points crowded together in some parts, and scattered in others. These disturbances being due to our atmosphere, it follows that if the telescope be made to follow the motion of a heavenly body, an exposure other than instantaneous must, to a greater or less extent, render every point of it a confused disc, and that therefore a photographic image will never be so perfect as the optical image given by the same telescope until instantaneity be secured.

'Notwithstanding, however, the disadvantages under which a photographer labours, I have obtained pictures of celestial objects showing details which occupy a space less than two seconds in each dimension. I might, I think, say even one second. Now 1 second = $\frac{1}{200}$ of an inch on the collodion plate, a second on the lunar surface, at the moon's

mean distance, being about 1 mile. The lunar picture in the focus of my telescope is about $1\frac{1}{10}$ inch diameter, but this varies of course with the distance of our satellite from the earth. . . . .'

De la Rue then stated that he considered a magnifying arrangement attached to the telescope as impracticable to secure good pictures, owing to the increase of exposure that would be necessary, and the consequent defects due to atmospheric disturbances. He considered that the enlargement ought to take place after the negative is taken.

He then describes the adjustment of the motion of his telescope to the lunar motion, which he effected by altering the length of a conical pendulum or friction governor, which altered the time of its rotation (or double beat). He proposed to effect the same alteration by another plan, which he subsequently adopted.

De la Rue at first obtained his lunar pictures in his 13-inch reflector by placing the sensitised plate at the side of the tube opposite the diagonal reflector, the light being thus twice reflected. Subsequently he obtained pictures directly at the focus of the mirror, which did not give him that increased rapidity of exposure which he had conjectured would result. He states: 'I am inclined to infer that Steinheil's result, as to the loss by reflection of the luminous ray, does not hold good as regards the actinic ray.'

He next compares the advantages of the reflector over the refractor, the principal one being that the foci of the actinic and visual rays are coincident.

'The time occupied in taking lunar pictures varies considerably. It depends on the sensitiveness of the collodion, on the altitude of the moon, and the phase. I have recently produced an instantaneous picture of the full moon, and usually get strong pictures of the full moon in from 2 to 5 seconds. . . . . The moon, as a crescent, under like circumstances, would require about 20 to 30 seconds in

order to obtain a picture of all the parts visible at the dark limb.

'Portraits of the moon equally bright optically, are by no means equally bright chemically; hence the light and shade in the photograph do not correspond with the light and shade in the picture; and hence the photograph frequently renders visible details which escape optically. Those portions of the moon near the dark limb are copied photographically with great difficulty, and it frequently required an exposure 5 or 6 times as long to bring out those portions illuminated by a very oblique ray, as others apparently not more bright when more favourably illuminated.'

In the practical instruction for the photography, De la Rue lays down that the silver bath must be as nearly neutral as possible, that cadmium iodide is the best iodiser to use with the collodion, and that the pyrogallic acid developer should be employed. For lunar photographs there can be no doubt that if they are required to be enlarged, iron development should not be attempted, since the deposit becomes too granular; but the writer is inclined to think that the rapid bromide emulsion plates developed by the alkaline method will furnish pictures which are equal to those produced by the wet method as described above, and certainly give a great decrease in exposure.

Mr. Rutherfurd at a later date having tried an 11½-inch refractor of the ordinary type, and also a 13-inch reflector, finally constructed a refracting telescope in which correction was made only for the chemical rays, and with this instrument he has produced some of the finest pictures of the moon which have ever been taken. With the great Melbourne reflector, however, photographs which are nearly perfection have been obtained, and there seems even yet to be a balance of opinion in favour of the reflector as against the refractor for this kind of work. Undoubtedly, where absolute coincidence of foci of all rays can be secured, all

other conditions being the same, the best photographs ought to be obtained. In lunar photography an unfavourable condition of the atmosphere is undoubtedly the greatest difficulty to be encountered. In a climate like England the air is rarely steady enough for the purpose. In countries which are more favourably situated as regards hygrometric conditions the difficulty is much reduced. In 1874-5, whilst the writer was in Egypt, Sir A. Campbell and himself had an opportunity of taking some lunar photographs with a refracting telescope of 7-inch aperture belonging to Mr. W. Spottiswoode. On the nights that the experiments were made really excellent negatives were obtained, which bore enlarging to 12-inch diameter. The apparatus employed was extemporised, and therefore of a rather rude description, but quite sufficiently true to give an idea of the excellent pictures that might be taken in such a climate with the appliances usually adopted for such work.

The photography of the planets has not as yet yielded anything of great value. Mr. Common and others, however, have obtained excellent pictures, though necessarily small, of Jupiter, Saturn, and some others. No doubt before long there will be a stride taken in this branch of photography which will render its universal adoption by astronomers a necessity.

In the earlier editions of this work it was stated : 'Photographing the stars is more a feat of photography than of practical utility in the present state of our knowledge, though at some future time it may be possible to map the heavens more thoroughly by its aid than has at present been done.' The prophecy which was then made is being amply fulfilled. The Brothers Henri of the Paris Observatory in France, Mr. Common and others in England, and Mr. Gill at the Cape of Good Hope have not only shown that stellar photography is something more than a feat ; but that it is the most ready means of mapping the heavens, and of ascertaining the star magnitudes in a way which was before

impossible. There is a divergence of opinion as to whether a reflector or a refractor is the better instrument to employ for this purpose; our own opinion tends to the use of the former. By means of photography stars which the eye cannot see in the telescope have been made to impress their images on a sensitive plate, since, with photography, time is a function which is as important as the brightness of a star.

Mr. Isaac Roberts has used photographs of the midnight sky to discover the position of minor planets. During the exposure of a plate the telescope accurately follows the motion of the stars. The apparent motion of the minor planets differs slightly from that of the stars; hence, while the latter leave small points on the plate on development, the former leave a linear track. This observer has also photographed nebulæ with which astronomers were unacquainted, showing that our knowledge in this direction may be increased by the use of the sensitive plate.

Regarding the photography of nebulæ there is a classic series of photographs by Mr. Common of the great nebula in Orion, a series which is not only interesting but important, as it will be a standard by which to compare others taken in future years.

Comets have been photographed and even meteorites, so that in the scientific study of the heavens it cannot be doubted that photography will play an even more important part in the future than the eye has done in the past.

CHAPTER XL

PHOTOGRAPHY WITH THE MICROSCOPE

PHOTOGRAPHY from a very early period of its existence has been utilised for securing accurate drawings in monochrome of what the eye can see in the microscope. This branch of the art is excessively fascinating, and can be worked in any leisure moments, either by day or night, when the enlargement is limited to say 50 diameters; but in order to secure images of greater dimensions it is always advisable to employ sunlight. The apparatus required is not very extensive. An ordinary microscope with say $\frac{1}{4}$-inch and 1-inch objectives and an A eyepiece is all that is necessary as far as the instrument itself is concerned. If the objects to be photographed are mounted on a slide, and not merely placed in a cell for examination, any ordinary camera may be attached to the microscope, as the tube can then be brought into a horizontal position. It has often been recommended to employ a camera as much as 6 feet in length, in order to secure great increase in the size of the object, but in the writer's experience it is unwise to go beyond 18 inches, a length just sufficient to enable the operator to grasp the slow-motion focussing screw, whilst his eye can be directed to the focussing screen. When the longer camera is employed, the operation of focussing has to be conducted by an assistant, and, however intelligent the latter may be, it will always be found that greater accuracy will be obtained by the operator's own hand, for it must be recollected that the difference of $\frac{1}{1000}$ of an inch in length of focus may determine whether the definition is good or bad.

The camera and the microscope should not be attached rigidly to one another. It is far better that each should be free to move independently, though care should be taken, when an accurate focus is obtained, that each shall occupy a perfectly unalterable position during exposure. Perhaps the most simple way of attaining this object is to substitute for the ordinary photographic lens used with the camera a short brass tube, which screws into a flange. A piece of velvet should then be formed into a cylindrical bag, open at both ends, and a little longer than the brass tube above referred to. If each opening of the bag is provided with an elastic band, a perfectly light-tight junction between the tube and the body of the microscope may be made.

Some operators prefer to use the eyepiece as a magnifier; it seems better, however, simply to employ the objective. If the objective only be used, it is wise to unscrew the tube of the microscope, in order to secure a larger field, which otherwise the diameter of the tube would limit. It must not be inferred that the use of the eyepiece as a magnifier will cause indifferent pictures in every case. In the instrument used by the writer the definition given by it was certainly bad.

The student is recommended to commence with a comparatively low-power objective. The 1-inch will be suitable in every way; and whenever he has obtained mastery over the manipulations with it, he may venture on the $\frac{1}{4}$ or $\frac{1}{8}$ inch. A higher power than these can seldom be recommended; probably the $\frac{1}{4}$ inch is the highest power which can be worked with ease. The tube of the microscope should be placed in an accurately horizontal position, as should also the camera; and care should be taken that the axis of the tube fixed in the latter should be in the exact continuation of the axis of the lens. This can only be effected by very careful arrangements. As a rule it will be found that when the body of the microscope is in a horizontal position the friction on the axis on which it turns is

sufficient to cause it to remain in the position in which it is placed; if not, obvious precautions must be taken to prevent any movement between the time of focussing and exposing the plate. Supposing that sunlight is to be employed for the purpose of illuminating the object, the next operation is to throw the image of the sun by a condenser on the object, in such a manner that the axis of the condenser and that of the objective may be in a line with one another. This may readily be ascertained by noticing the illumination when no object intervenes between the rays emerging from the condenser. It is advisable, first of all, however, to place the heliostat (the one described at p. 323 answers the purpose) in position. This can be done with sufficient accuracy by rough observation with the eye, and noting that the centre of the mirror is about the same height, and in the same horizontal line, as the tube of the microscope. The condenser is then brought into the reflected rays, and an image of the sun brought to a focus on the object. In some cases the heat rays have to be cut off, otherwise injury to it ensues. A glass cell with parallel sides containing well-boiled distilled water is found to subdue the heat sufficiently when placed in the path of the beam. The focussing is now proceeded with, and is best performed by removing the ordinary ground glass, and substituting for it a sheet of ordinary patent plate, viewing the image by a focussing glass, as described in Photo-spectroscopy, p. 320. The portion of the object to be photographed should be brought into the centre of the field, and when nearly in position the slide should be clipped on to the stage by a couple of wire springs, and the adjustment effected in the usual manner. The absolute focussing should next be taken in hand. A rough approximation is first obtained by the rack and pinion motion, and the final focus obtained by the slow-motion screw, which is attached to every good microscope. When viewing the image through the focussing glass it will

be found that in no position is the object quite free from colour. In one focus it will appear sharply defined, though surrounded by a red band, whilst the definition will appear equally good when in a different focus, when surrounded by a blue halo. These colours are due to a want of achromatism in the objective, and the *former* position should be chosen to obtain a sharp photograph; for since the blue rays are as a rule the most active in causing the photographic image to be formed, it is evident, if the latter focus, which is most accurate for the red rays, be chosen, the resulting picture will be blurred.

Monochromatic Light.—The fact that coloured fringes are sure to border the image shows at once that the objective is not properly corrected, and there would evidently be an advantage were it possible to work with monochromatic light. This can be accomplished in the following manner. In fig. 123 RR are rays coming from a heliostat or other source of light, and an image of the source (or in the case of an artificial light, an image of the condenser) is formed on the slit S_1 of the collimator C by the lens L_1. The parallel rays produced by the lens L_2 pass through the two prisms P_1 and P_2, and are focussed by a lens L_3 on to the screen D, in which is a slit S_2, forming a spectrum on D. The rays which pass through S_2 are again collected by a lens L_4, and an image of the surface

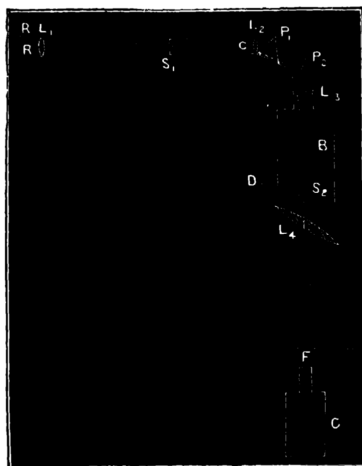
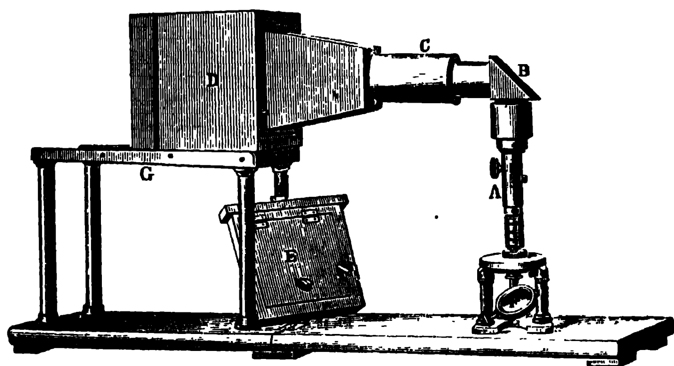


Fig. 123.

of the second prism is focussed on the object on the stage of the microscope. This gives monochromatic light, and according to the kind of plate used for photographing the object, so is the slit S_2 moved into that part of the spectrum to which it is most sensitive. L_1, L_2, L_3 may all be of about 9 inches focal length, and L_4 considerably shorter. There is no need to have these lenses achromatic ; ordinary spectacle lenses may be made to answer.

The photographic delineation of opaque objects is much more difficult to accomplish than that of those which can be examined by transmitted light. The difficulties will be found to increase rapidly if any endeavour be made to use a higher power than a $\frac{1}{4}$-inch. The same arrangement as that indicated may be employed, causing, however, the rays to fall on the object. This gives a very feeble illumination, and with great magnifying power the difficulty of focussing is excessive. When once a focus is obtained all difficulty vanishes, and by the use of dry plates any amount of exposure may be given without any deterioration of the image.



The above figure shows an arrangement by which a microscope may be employed in its ordinary vertical position.

The instrument was in the Loan Collection of Scientific Instruments at South Kensington, and is of German make. The form of the camera might advantageously be altered to a bellows shape. A is the microscope; B a right-angled prism reflecting the rays of light which pass through the objective into C, a brass tube fixed to the camera D. E is the dark slide. The length of the camera is supported by two iron rails G. It will be noticed that the same method of illumination can be applied in this position of the microscope as when it is used horizontally, for the rays of light can be reflected by the mirror F.

Hitherto we have only supposed the student to be working with sunlight, but, as may already have been inferred, artificial light may be employed. The great desideratum with the latter is that it should be steady, and should proceed as nearly as possible from a point. The light from a magnesium lamp has been recommended, but in the writer's experience it is most unsatisfactory. The electric light is good, but is somewhat difficult to manage, though, owing to the intensity of the illumination, the time necessary to keep the points in proper adjustment is not very great. The limelight, perhaps, possesses the greatest advantage over all lights, since it is so perfectly steady. A gas flame, a paraffin lamp or even a candle may be used where very great enlargement is not required, now that plates are obtained which are so sensitive as those prepared by the gelatine process; and no doubt the majority of microscopic objects are at present photographed with one of these sources of illumination.

The use of photography with the microscope has not as yet been fully developed, but there can be no doubt that as more workers enter into this field the greater will be the advances made.

CHAPTER XLI

THE FAILURE OF A PHOTOGRAPHIC LAW

We must here deal at some length with an effect of light which is, if not unexpected, at least contrary to what is the generally received opinion.

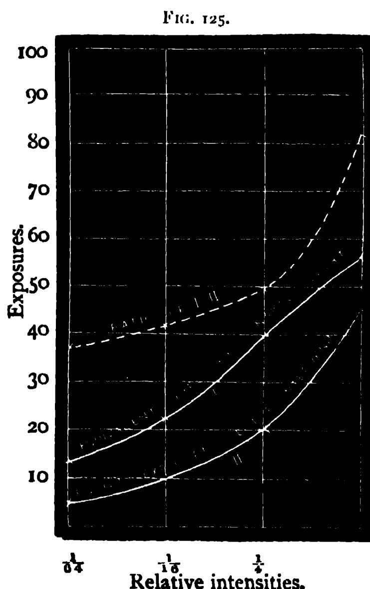
The writer had often suspected the failure of the assumption made that on the same sensitive surface, when the product of intensity of light and time were equal, the chemical action must be the same. In his presidential address to the Mathematical Section of the British Association in 1889 he expressed his suspicion in this matter. And again in his address to the Photographic Society on November 8, 1892, he repeated his conclusions. In this latter he said: 'And I would point out that up to the present time it has been held that if time and intensity of light gave a certain chemical change in a body, then the same would be produced if the two multiplied together gave the same constant. . . . When we get intensities of light which are almost infinitely feebler than those with which we are accustomed to deal, the "time into intensity" law will be found to break down.'

Effect of Intermittence of Exposure

The first experiments made by the writer on this subject were based on a difference which was observed in the amount of chemical action obtained from a continuous and an intermittent exposure, the time during which the sensitive surface was exposed being the same in both cases.

Suppose we have the amplitude of the swing of an atom of a molecule increased by the impact on it of a ray of light, and further suppose that the light is suddenly shut off, the tendency of the atom will be to revert to its normal swing; if we again admit the ray of light for another brief interval, the atom will again increase in its swing, but perhaps just not sufficient to allow it to swing away from the attraction of the molecule. The swing or amplitude attained by the atom will not be so great as it would be when the two exposures were combined into one, for in the latter case there would be no falling back towards the normal swing. In the first case, then, the atom might not leave the molecule; in the last case it might do so. The minimum number of exposures have been supposed for simplicity's sake, but the same arguments hold when the exposures are increased.

Fig. 125.



To make the experiments it is convenient, though not necessary, to have a special slide which will enable any number (within limits) of exposures to be made on the same plate. In the latest pattern of slide used by the writer the front is pierced with six holes, all, or any one, of which can be covered up at pleasure.

A striking result in intermittent exposures was ob-

tained with a gelatino-bromide lantern plate. Two sets of exposures were given at different distances from the source of light. Exposures at each distance were made (1st) with the naked light and (2nd) with a rotating sector intervening, having twelve apertures of 5° each; the exposure in the second case had to be, therefore, six times longer than in the first case, to make the total exposures equal, for the total number of apertures was only equal to 60°. From the note which the apertures gave when a current of air was projected against them it was found 720 exposures were given per second.

Fig. 125 shows graphically the results.

The apparent loss of exposure by the intervention of the sectors increases as the actual intensity of the light diminishes, the ratios of the single exposures to that of the intermittent being:

For intensity	1	... ...	1 to	·815
,, ,,	$\frac{1}{4}$	... ...	1 ,,	·500
,, ,,	$\frac{1}{16}$	... ...	1 ,,	·423
,, ,,	$\frac{1}{64}$	... ...	1 ,,	·370

Tabulated results.

Scale taken at 3 feet		Distance in feet	Relative Intensities	Exposure	Reading of Transparency	Comparative Chemical Action derived from Scale	Ratio of the Unbroken to Sectorial Chemical Action
Exposure	Reading of Transparency						
Sec.				m. s.			
5	87·6	$1\frac{1}{2}$	1	0 10	27·8	56·4	·815
10	75·3	$1\frac{1}{2}$*	1*	1 0*	33·3*	46·0*	
20	55·0	3	$\frac{1}{4}$	0 40	37	40	·500
40	37·0	3*	$\frac{1}{4}$*	4 0*	55*	20*	
80	18·0	6	$\frac{1}{16}$	2 40	53	22·2	·423
		6*	$\frac{1}{16}$*	16 0*	76·5*	9·4*	
		12	$\frac{1}{64}$	10 40	69·5	12·7	·370
		12*	$\frac{1}{64}$*	64 0*	88·8*	4·7*	

The figures with an * beside them are those which relate

to the exposure with the sector. The ratio of exposure to rest is 1 : 5.

What shape the curve of these ratios would assume when the intensity of the light is greater or less than that shown can only be guessed at. We have thus arrived at the conclusion that the sum of small exposures is not equivalent to one exposure for the same length of time.

Now the question arises whether a long rest after a short exposure, and then another exposure and again a long interval of rest, is conducive to minimise chemical action. The reasoning is not difficult when we take the same lines as we took in our last argument. A long interval of rest after a short exposure must inevitably give a longer time to those atoms which are not swung out of the molecules to come back to their original swing; hence, the shorter the time of exposure is to the time of rest, the less chemical action there should be. This was tested experimentally.

The effect of varying the length of each individual exposure, the ratio of interval of exposure to that of rest remaining the same, was also found by experiment.

The result showed that apart from any influence that ratio of the time of exposure to the time of rest may exercise, the absolute duration of exposure affects the result. When, as in this case, the absolute duration is 200 times greater in one than the other, the chemical action is rather more than double.

It was also found that the length of the interval which elapses between successive and equal exposures has an effect upon the apparent exposure, but it became necessary to trace the result when *the exposures were equal in length, but the intervals of rest between such exposures differed* in amount. An experiment was made, and the curve obtained showed that as the number of apertures in the sector was diminished the less did the chemical action become.

These experiments will be found fully detailed in 'Light in Photography,' chap. xii.[1]

Effect of Small Intensities of Light

From these experiments the writer proceeded to determine the effect of small intensities of light upon the photographic plate. When a plate is exposed for a certain time to a light of given intensity, we say commonly that a plate has received so much exposure. If the time is altered and the intensity also, so that the exposure (time multiplied by intensity) is the same, we have been taught that the same chemical effect will ensue, or, to put it in other words, the exposure will be the same. Now, as a matter of fact, this is not true in every case, though it is true for the conditions under which a photographer usually works. We have in our sensitive salt the atoms composing it vibrating, and when light acts on it we have the oscillations increased and the amplitudes greater. We can scarcely conceive that there should be any great difference of effect produced by a series of impulses of a certain strength prolonged over a certain time, and a series of impulses of a fraction of that strength lasting over a proportionally longer time. Yet there is a difference, as experiment shows. A perfectly satisfactory explanation of this deviation from what might be expected is at present wanting. We may, however, look upon the matter in the following way. Suppose we have a series of waves of light falling on a particle, which is, of course, composed of an almost infinite number of molecules, and that in the oscillation of these last some one atom feels the impact of one wave of light, and the extra swing so given is just able to send it off from its mother molecule, then that molecule will be liable to decomposition by the developer. Now supposing we have

[1] *Light in Photography*, by Sir W. de W. Abney, K.C.B. (Sampson Low, Marston & Co.).

a series of waves carrying half the energy, it might be supposed that it would require two of these blows to send the atoms away from the molecule; but it by no means follows that the *same* atom would receive the second blow. Some other atom might be in the line of the waves and get the blow instead, or, if the original atom received it, it might not be in that part of the swing which would render the blow most effective. In either event the atom would not leave, but would be kept in the group of the mother molecule.

In the case cited the intensity of the light in the first would be double that of the second, but the time of exposure would only be half that of the other. It will be noticed, of course, that this explanation depends on the fact that a certain amount of 'light energy' has to be expended in separating the atoms from the molecules.

In the following experiments, which are culled from the original papers in the 'Photographic Journal,' vol. xviii. p. 56, the source of light most usually employed was an amyl-acetate lamp, known as the Siemens unit light, as any variation in it is excessively small. The point to attend to is to light the lamp some ten minutes before it is to be used, and adjust it so that the tip of the flame just reaches the gauge pointer. After this period it will remain at the same height almost as long as any amyl acetate remains in the reservoir. Every part of the flame could always be seen from each part of the surface exposed.

In the first experiment the sensitive surface was bromide paper of medium rapidity. Small squares on a quarter-plate size of this sensitive material were exposed at different distances to the amyl-acetate lamp. The times were calculated so that the product of intensity and time ($I \times t$) was a constant, however much I or t varied, which in accordance with the assumption usually accepted should give equal chemical action as shown by the blackness on development, I being the intensity of the light and t the

time of exposure. A scale of exposures was added on the same paper by exposing different parts for known times,

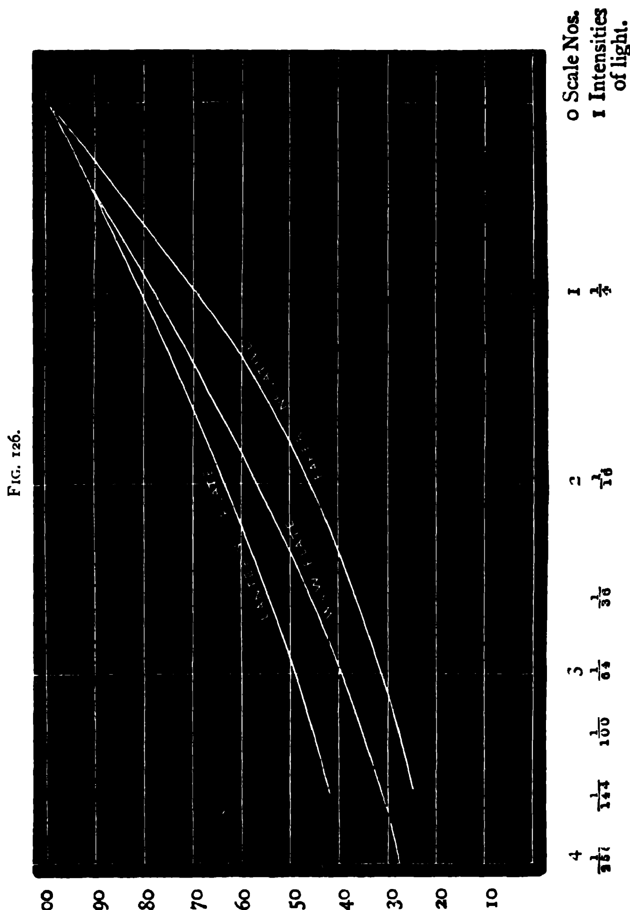


Fig. 126.

the distance of the lamp remaining constant. The paper was then developed carefully and fixed. When dry the

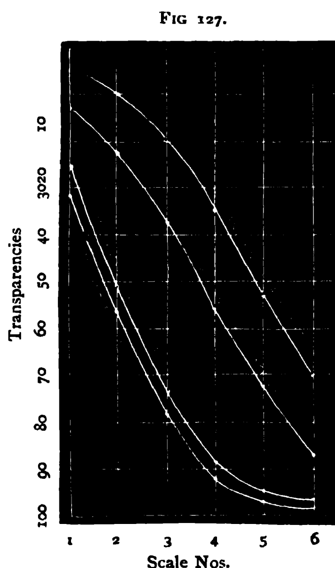
scale of blackness was measured, as was also the blackness of the small squares, which had been exposed at different distances, and the latter referred to the former.

The measurement of the greyness produced was made in the instrument, fig. 115. The lowest curve in fig. 126 gives the results. If there were no alteration in chemical action the curve should be a straight horizontal line.

As a fact, the energy usefully expended at 24 feet was less than a quarter of that expended at 2 feet on the sensitive surface, although the time of exposure was proportionally lengthened to make the intensity and time a constant.

A lantern plate, more sensitive than the foregoing paper, was similarly treated as in the last exposure, and the top curve in fig. 126 shows the results. The energy usefully expended at 24 feet was only two-fifths of that expended at 2 feet.

FIG 127.



The foregoing are decidedly 'slow' sensitive surfaces. The next experiment was with one of Wratten and Wainwright's plates. The amyl-acetate flame was reduced in height, so that the result does not absolutely compare with the two former. Here the energy usefully expended at 24 feet is only a quarter of that expended at $1\frac{1}{2}$ feet. The results are shown in fig. 126.

By using a Spurge's sensitometer (see p. 347) it was proved that the differences were not due to atmospheric absorption (see fig. 127).

Another series of experiments was undertaken to ascertain if there is any difference in the gradation when different intensities of light were employed at *fixed distances, and progressive times of exposure* were given, so that time multiplied by intensity was kept the same.

Examples with a slow lantern-plate and a quicker plate are given as indicating the results always obtained. They were exposed to a light at 2 feet and 8 feet, the times of exposure being 1 to 16. Fig. 127 gives the plotted curves, and each pair of curves are parallel. The 'gradation' is therefore practically the same.

We may sum up these results so far as to say that with slow and moderately fast plates the intensity of the light acting on a plate alters its apparent rapidity in a very marked manner, but the alteration is smaller as the rapidity of the plate increases, until with a very rapid plate no practical alteration is made at all.

The intensities of light we have considered are moderate ones, and when we come to very intense lights the conditions and the results are changed. The camera image is formed by different *intensities* of light and a fixed time exposure. It follows that the gradation of some plates will be different in the camera from what it would be if the image were impressed by varying the times of exposure.

Action of Very Intense Light on Plates

The results obtained when very intense light acts upon a plate approximate to those found with very feeble intensities—that is, that the chemical action produced is lessened for a constant exposure (time multiplied by intensity) when the light is very intense, and that consequently there is some one intensity which will give the greatest chemical action. We must recall our former picture of the atomic swings to form an idea of how this may occur. The removable atoms are swinging with their

ordinary swing, and a series of waves of light of great amplitude fall upon them. Let us suppose that the passage of two waves through the space occupied by the molecule is sufficient to destroy it by swinging out one of the atoms. Now let us double the energy carried by the waves; then the energy of one wave ought to be sufficient to cause the same effect, but the one wave would pass through the space in exactly half the time that the two waves took. The chance that the atom was at such a period of its swing that the energy could be properly applied to effect this result would be half in the latter case that in the former. The same kind of result would obtain with a larger number of waves.

In the case of low intensities the chances of a 'hit or miss' of an atom by a wave are the same, but with them we have to use the argument that a large number of blows is necessary to increase the swing to shift the atom from the molecule, whilst with high intensities the number of blows is reduced to a minimum, and the times in which the blows can be given are proportionately reduced. An investigation of this kind will show that there is some one energy due to wave motion that will in a given time decompose the greatest number of molecules.

If we take Helmholtz's explanation of anomalous dispersion, and apply it to our molecules in this case, we have a viscosity or resistance to motion to deal with. If we suppose that a comparatively heavy blow given to an atom will not give the full swing to it that it would take supposing there were no resistance to the motion, we can conceive that with a still heavier blow the resistance would be further increased (somewhat in the same way that atmospheric resistance to the passage of a body increases more rapidly than the velocity), and the length of swing given would be proportionately curtailed.

Thus, if an atom received two blows, one double the energy of the other, it is possible that the blow of double

energy would not increase the swing of the atom to the extent it would reach from two blows of the other.

This being the case, there would be some amplitude of wave which would give the greatest effect, while exposure (time multiplied by intensity) remained constant.

It is not proposed to give many experimental details: the original papers in January and March 1894 of the 'Camera Club Journal' should be consulted if more are required.

If by any means we can get deposits produced by varying intensities of light acting for such a short period of time as the $\frac{1}{50}$ of a second, and then produce others by feebler light but having the same proportional variation in intensity, we can compare the two gradations of transparency with great facility. We can make a scale of varying transparencies (*i.e.* to allow different intensities of light to pass) by exposing a plate to an amyl-acetate lamp for varying times and developing it. The deposits will allow different intensities of light to pass to a plate which is in contact with it.

We can measure the light transmitted by this scale of transparency by the method given before, and if the method of development has caused a jet-black deposit the optical value and the photographic value of the density will be the same.

Having got a scale, the next point to arrange is to give a short exposure. In the first experiment that will be described this was accomplished by utilising an extemporised drop-shutter.

The shutter was placed close to the scale, with the aperture parallel to its length. The plate was in contact with the scale. An electric light of some 1,000 visual candle-power was placed 5 or more feet away from it, the necessary distance being found by trial. An exposure was given, the time of the passage of the aperture in the shutter over the scale being measured. Other exposures through

the same scale were given on different parts of the plate to the comparatively feeble light of an amyl-acetate lamp placed at 3 feet 6 inches from the negative for varying times. It must be remembered that in all cases the variations in the intensities of the light passing through the scale were in the same proportion. After development we have upon the same plate an electric-light exposure and several amyl-acetate lamp exposures. (Although the visual intensity of the electric light is only 1,000 candle-power, yet photographically it is at least equal to 10,000 candles.) From these last we can pick out two—one in which the opacity given by the passage of the light through the most transparent square of the positive is nearly that given by the passage of the electric light through the same square, and the other in which the opacity of the most opaque squares is the same. In all cases, even with the most rapid plates that were tried, the gradation given by the electric-light exposure was much more gentle than that given by the amyl-acetate. The following are two examples of this and are noteworthy—one is a Barnet plate (ordinary) and the other an Edwards plate (special rapid) (see fig. 128). 1st. For both plates the amyl-acetate lamp was placed at the same distance from the standard scale of density, and in both cases one of the exposures selected and measured was for 30 seconds. By the method of determining the comparative speeds of plates which was proposed by the writer at the Camera Club Conference, 1893, the Barnet plate from this exposure is about 2·9 or 1·9 times more rapid than the Edwards plate. 2nd. The Barnet plate was exposed through the scale at 4·5 feet distance from the electric light, whilst the Edwards plate was exposed at 8 feet. This makes the intensity of illumination given to the Barnet plate $\frac{64}{20{\cdot}25}$ or 3·11 times more than to the Edwards plate. The electric (arc) light was giving out approximately the same amount of light in both cases, and the time of exposure was also the same. Had they both

received the same exposure in this case, the rapidity of the Barnet plate would have been almost exactly twice that of the Edwards plate, but it received about three times more

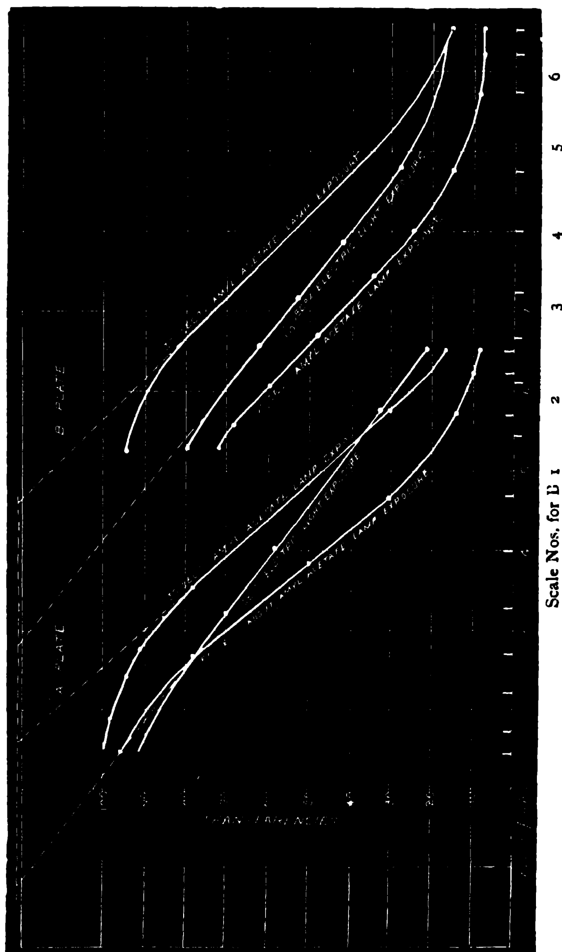


FIG. 125.

light. The Edwards plate is therefore 1·5 times more rapid for intense light than is the Barnet, though with the low illumination the Barnet is about twice as rapid as the Edwards plate. This appears to indicate that the relative rapidities of plates may alter according to the intensity of the light in which they are employed.

Further experiments were carried out, in which not only was the amyl-acetate lamp and the electric light used, but the electric spark, the intensity of which must be many times greater than sunlight, was employed. The spark was taken between the terminals of a spark-gap apparatus, the knobs being usually $\frac{1}{3}$ of an inch apart. One terminal was in connection with the inside and the other with the outside coatings of five Leyden jars, which were charged by a Wimshurst machine. The machine was worked till the spark passed across the gap, the plate being exposed through the graduated screen to its action; other portions of the plate were exposed to the action of the electric light and of the amyl-acetate lamp as before described, and a 'time scale' of density was also impressed by the amyl-acetate lamp. Similar experiments were carried out with other plates, and in all cases the results showed that the more intense the light within the limits used the less steep was the gradation.

Another set of experiments are full of interest: they demonstrate that *if the intensity of the light is increased beyond a certain limit, the product of intensity and time being kept constant, the energy used up in the work of chemical decomposition diminishes.* The first experiment that was made was with a snap-shot plate, exposed naked at 18 inches and 12 feet respectively. The writer was not prepared for the enormous difference in results; the one spark showed but a feeble deposit, whilst the exposure at 12 feet distance to 64 sparks caused opaqueness. Another plate (an Ilford ordinary) was exposed (without any graduated screen intervening) at 12, 9, 6, 3 and 1½ feet distance,

and the illumination of 64, 36, 16, 4 and 1 sparks—the equivalent number of sparks—was given at these respective distances. A time scale was also impressed on the same plate and the whole developed together. Now, although the *absolute* equivalent exposure cannot of course be told by applying the measures of transparency given by the spark exposures to the measures of the time scale, yet their *relative values* can be. Taking the result of the exposure at 12 feet as 1, that at 9 feet is ·87, at 6 feet ·72, at 3 feet ·41, at 1½ feet ·22.

This shows that there is apparently less than a quarter of the energy usefully employed in producing chemical action at 1½ feet as compared with that at 12 feet, a result which seems somewhat marvellous. It might be thought that this result was due to 'reversal' of the image, but other experiments proved that it was not so. Several brands of plates were experimented with, and the same results were invariably obtained.

So far the action on rapid plates has been described, but to make them more complete slower plates were experimented with. A slow lantern-plate was exposed at different distances with an equivalent number of sparks, and the results were instructive. Although the exposure at 1 foot appeared a little less than at 8 feet, there is far less difference than when the quicker plates were used. This is what was to be expected. In the previous experiments it was shown that with these plates the energy expended with feeble intensities and equivalent exposures was much less than with stronger intensities, whereas with the rapid plates there was not much difference. The rapid plate must, therefore, evidently arrive sooner at the point where the energy expended was at its maximum than would the slow plate.

Combining these experiments, we are able to deduce the fact that for every plate there is an intensity of light which has a maximum effect upon it with a given exposure, and that on either side of this maximum the useful energy decreases.

Effect of Temperature on Sensitiveness

A plate covered with calcium sulphide (Balmain's luminous paint), exposed to a fairly strong light for a second or two, will be found to glow when taken into a dark room. If a warm flat-iron be applied to the back of the plate while it is glowing, the part warmed will at once increase in brilliancy. Remove the iron, and the surface of the plate will after a short time become of equal brilliancy throughout, and after a further lapse of time the portion which was warmed will become darker than the rest of the plate. The heat of the iron causes the molecules to oscillate more violently than those adjacent to them, and there is an increase of phosphorescence, but at the expense of the energy stored up. It follows that when the heat is withdrawn (or, indeed, the same thing would occur if the iron were still kept in contact with the plate), the light energy at that portion having been largely consumed, that part rapidly becomes darker than the surrounding portions.

A further experiment will show that the hot iron has not imparted fresh energy.

If the hot iron is applied in the dark room to a plate similarly coated but not exposed to light, the darkness of the plate will be unaltered. The heating effect stirs up the molecules to greater motion, and sensitive salts should under such circumstances be more sensitive when heated than when exposed at ordinary temperature, for what is true of one kind of matter ought to be true for another.

If a hot flat-iron is pressed against the back surface of a gelatine bromide plate in daylight the colour of the sensitive salt will alter, becoming deeper, and on the plate cooling it resumes its natural colour. Iodide of silver in intense cold changes to a grey tint. Such changes of colour mean something, and that 'something' ought to show itself when these sensitive compounds are exposed.

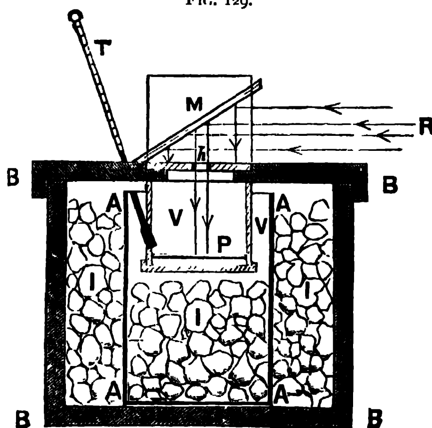
If we heat a portion of an ordinary sensitive plate, and expose the whole of it to the same light and develop, we can see at once if the hot portion is more sensitive than the cold. The plate may be covered with black paper and the hot iron applied, after which the plate should, while warm, be exposed to a feeble light. If developed immediately, it would be correctly said that the part of the plate which was warm would heat the developer and make it more active. To guard against this the plate should be laid on one side till quite cool. On development the image of the iron will be perfectly evident by increased deposit, indicating that the increased temperature during exposure has increased the sensitiveness. As it might be thought that the heat has permanently increased the sensitiveness, the experiment may be repeated, but in this case the plate should be allowed to cool *before exposure.* On development there will be no trace of any action of the heated iron. In working with collodio-bromide emulsion, with which a trace of moisture is necessary in the film, the hot iron cannot be used; but if the plate is wetted all over in cold water, and one end dipped into hot water, similar effects may be obtained.

It seems, then, that by increasing the temperature of the sensitive surface we increase the sensitiveness. The converse of this should also be true. For experimental proof, if the dark room be warmed to about 90°F., and instead of heating the flat-iron it is immersed in a mixture of pounded ice and salt, the metal will acquire a temperature considerably below freezing-point. When thus chilled, if placed in contact with the back of the plate, which has the temperature of the warm room, an exposure as before should be made to the feeble light. When the cold part of the plate has recovered the heat it had lost, it may be developed, and it will be found that the image of the iron is less dense than the surrounding parts, and consequently it may be assumed that the

plate has become less sensitive by the lowering of the temperature. Similar experiments carried out with daguerreotype plates will dispose of any idea that the lowering of the temperature was due to the water in the gelatine being frozen.

Professor Dewar found that the speed of a film at the low temperatures of −180° to −200° C. was reduced to at least a quarter of what it was at ordinary temperatures; and the writer, in a communication to the Camera Club, gave evidence that between the temperatures of 100°F. and 0°F. the speed of a rapid plate was reduced even more.

FIG. 129.

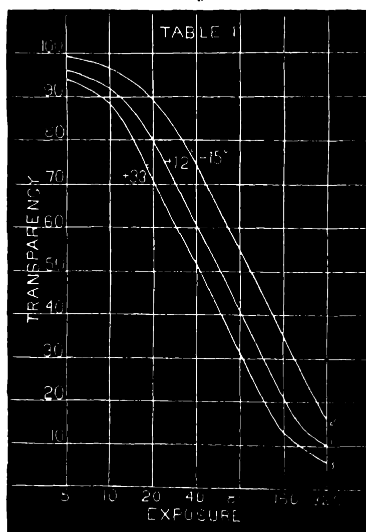


Having arrived at a definite conclusion by means of qualitative experiments, the writer turned his attention to devising quantitative experiments, with a view of forming some idea of the increase and diminution of the sensitiveness by known heat and cold.

The method of exposure was as follows: The apparatus (fig. 129) used was a simple box, B B, with a smaller tin box, A A, when cold was required, inside it. Between the outer box and the tin was placed a mixture of salt and ice, I, which reduced the temperature of the box to 0°F., about. This was further facilitated by placing in the tin box a similar mixture up to a level which was regulated by the plate P. The plate was suspended in a pair of grooves cut in two stays, V V, which are pendent from the lid. In the lid a small hole was cut, to allow the bulb of a thermometer, T,

to be thrust to the level of the plate. A square hole *h* was cut in a sliding batten, which moved across a slot-like aperture cut in the lid, and over this was a mirror, M, supported at an angle of 45°, to reflect light vertically down from a horizontal beam of light R on to the plate. The source of light being at some distance from the mirror, the light impressed the plate with an image of the hole (in this case square), and as the hole was moved along horizontally so different parts of the plate could be exposed for different periods. The plate was exposed at the ordinary temperature of the dark room, next at —18°C., and then at about 34°C. This last was effected by removing A A, and heating the box by placing at the bottom a heated brick to keep the temperature constant during exposure.

FIG. 130

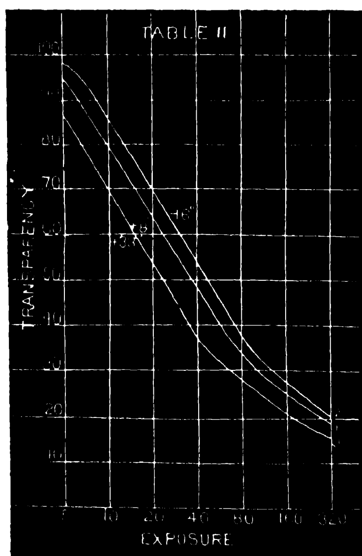


It would, of course, be useless to give details of every experiment made, but three examples are recorded: first of all where the temperature employed varied between 33°C. and about —18·5°C.

From the diagrams it will be seen that there is not necessarily any variation in the gradation of the curves—that is, their general slopes are usually parallel to one another, as might be expected, since the varying exposures are made by altering the time—but that the rapidity is altered, but not to the same degree, for each kind of plate.

In every case the rapidity is invariably less with those cold temperatures which the photographer sometimes meets with. The exposures were successively doubled, and for convenience these excessive exposures are made the scale of abscissæ. Thus 10, 20, 40, 80 seconds are shown as 1, 2, 3, 4, and the transparency of the deposit is shown on the vertical scale as ordinates, 100 being the total transparency. For a lantern plate (fig. 130) the distance apart of the 'hot' and 'cold' curves is 1·2 of the scale divisions, which implies, as each successive scale number means double the exposure of the previous one, that the chemical decomposition at $-16°$C. is $2^{1·2}$ times, or 2·3 times, less than that at $+33°$C. With the 'lightning' rapid plate (fig. 131) it is just double, whilst with a Fitch film (fig. 132) it is only $2^{·7}$ times, or 1·6 times.

FIG. 131.

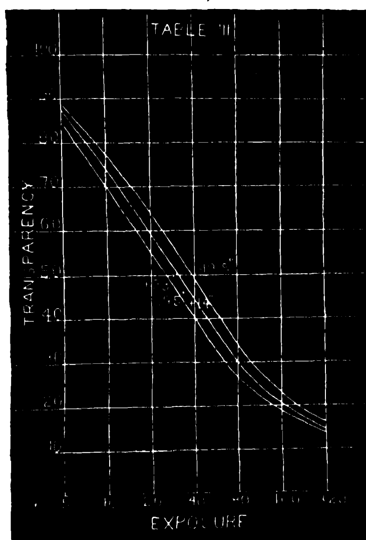


These numbers indicate that all degrees of sensitiveness are not equally affected. The 'lightning' plate and the slow-lantern plate are not very far off one another, but the film which is intermediate is so much less that there must be some reason for it. Whatever may be the cause, we find, however, that when time of exposure, multiplied by the intensity of the light, is a constant quantity, the chemical

action is different, and that the colder the surface is the less sensitive it becomes.

From experiments made with a collodio-bromide plate to ascertain the diminished rapidity between 17° C. and +32°C., it was found that the same opacity as was got with the hot exposure was only obtained when the cold exposure was increased by $\frac{149}{32 \cdot 6}$ or $\frac{74}{16 \cdot 3}$, or 4·5 times.

Fig. 132.



From a number of experiments made at temperatures ranging from −18°C. to +38°C., it was found that the curves were not parallel to each other—the gradation was altered In a further experiment, after the hot exposure had been made the plate was allowed to cool down, and before it had time to absorb moisture an exposure at the ordinary temperature was given, when *its curve became parallel to the 'hot' curve.* Evidently by heating to +38° we have something altered in the plate, which alteration remains after it is cooled for some little time—long enough, indeed, to allow another complete set of exposures to be made after the cooling is complete and before it resumes its normal condition. From this it appears that, up to 33°C. at all events, the heat has no effect on the plate beyond making it more rapid.

The natural and most probably correct conclusion to draw from this is, that at near 38° the water which is in the gelatine begins to be eliminated, and alters the condition of the film. At −18°C., or near zero F., it is quite possible that the amount of water present would be in a state that it would not freeze, but be left in semi-combination, so that it can take its usual part in combining with the halogen released from the sensitive salt during exposure.

The question of whether exposure to *different intensities* of light *for a fixed time* was equivalent to a fixed intensity and variable times was a matter which next called for attention, for it cannot be too well remembered that it is the former we have to deal with in a camera exposure, and not with a variation of time. There were some difficulties in carrying out these experiments, but they were gradually smoothed away. A scale, consisting of squares of gradation of known transparency, was laid upon the plate. The light was admitted through a thickness of blotting-paper, which took the place of a portion of the lid of the box, and thus equal illumination of the whole length of the plate was obtained. It was found in this case, as in all others tried, that the 'hot' curve was steeper than the 'cold' curve. To sum up these experiments, we see that the effect of heat is to increase the apparent rapidity of the plate with time exposures, and to increase the steepness of the gradation of the plate with different intensities of light.

Effect of Different Monochromatic Light on the Gradation

One other phenomenon must be noted, and that is the gradation of a plate is affected by the colour of the light which produces chemical action on the sensitive salt. Some years ago the writer alluded to this fact, and it was noticed

by Mr. Chapman Jones in regard principally to isochromatic plates. The writer was in the middle of his investigations at this period, and he has recently published in the 'Proceedings of the Royal Society' his quantitative results. Monochromatic light of different wave-lengths was used to form scales of gradation on bromide of silver, the exposures being altered in geometrical series either by varying the intensity of the light or by altering the time of exposure. It was found that in both cases the least gradation was given at the wave-lengths to which the salt was most sensitive, and that it increased in rapidity as it approached each end of the spectrum, the gradation in the red being steepest.

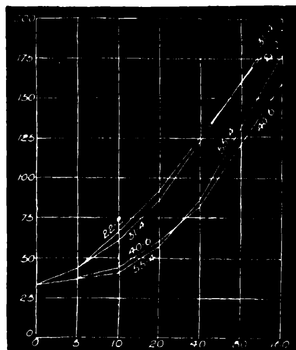


Fig. 133 shows one of the results, the ordinates being the *densities* of deposit on the —log of the transparency. 55·4 is in the red of the spectrum, 40·6 in the green, 31·4 in the blue-green, and 22·2 in the blue, the ray which has most effect on the salt used.

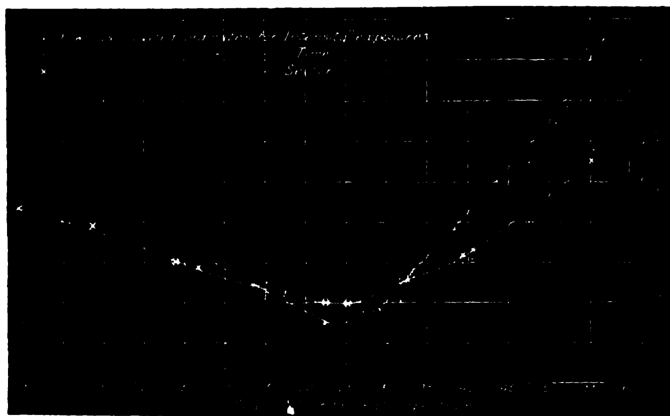
When experimenting with altering the time of exposure two methods were adopted: one the ordinary plan of shutting off an exposure at a given instant, and the other by rotating a disc in front of the plate in which were cut apertures round rings of the appropriate angles, and giving one exposure. The results of the measurements are shown in the accompanying fig. 134. The scale of ordinates shows the varying lengths of the scale of abscissæ which would be required to produce with the ray 22·2 the same density as that produced by the other rays. The

following are the scale numbers of the principal Fraunhofer line :

B 61·3
C 58·1
D 50·6
E 39·8
F 30·1
G 11·2
H 0·

It will be seen that the gradation varies more when the intensity of the light is altered, the time of exposure

FIG. 134



remaining constant, than when the time is varied and the intensity of the light acting remains constant. This is all in accord with the preceding sections, as the time necessary to produce an image, say, with the red is very prolonged. The outcome of this is, that, supposing we wish to get a vigorous bromide print from a very weak negative, we should illuminate it by red light, when vigour will be obtained.

We may here call attention to the action exerted by certain metals and other substances on the photographic plate.

Dr. W. J. Russell has investigated the phenomena observed when photographic plates have been allowed to rest in close proximity to printer's ink, metal plates, and other substances.

He found that if gelatino-bromide plates, bromide paper, or even gelatino-chloride paper, were allowed to remain in contact with dry hard copal varnish, printer's ink, and certain metals and other substances for periods varying with the sensitiveness of the plate or paper used and the activity of the substances experimented with, effects were produced which became visible by development in the ordinary way. All vegetable oils produced the effects, but with different degrees of activity. Linseed oil was one of the most active bodies, and olive oil the least so. Turpentine was very active, as were all the class of bodies known as terpenes; alcohol, ether, and water when pure had no effect. Various samples of printing inks differed widely in activity, the colour of the inks by themselves appearing not to influence the action, though blue ink was usually inactive; but this Dr. Russell attributed less to the colour than to the nature of the oil used in making it. Charred wood and charcoal were active, but when the latter was strongly heated in a crucible it lost its powers. Most woods retained their activity for long periods, and he cited the case of a piece of oak, a portion of a box which had been stored in a dry place for nearly a hundred years, and yet gave a good image. Passing to the metals, he found that magnesium was the most active, after which came cadmium, zinc, nickel, aluminium, lead, bismuth, tin, cobalt, and antimony. He early came to the conclusion that the active principle was a vapour, and was confirmed in his opinion by finding that when a plate was suspended film downward, with a perforated plate slightly separated from it, over a quantity of drying oil

the action took place most strongly opposite to the perforations, but also spread laterally in the same way that a vapour would. He found that films of gelatine, collodion, and gutta percha were pervious to the vapours, but that glass, mica, selenite, and gum arabic, when interposed between the active body and the sensitive surface, effectually stopped the action. Further experiments led him to the conclusion that peroxide of hydrogen was the active agent in all cases, and was by itself the most active of all substances. He gave instances where neutral substances which had been in contact with active bodies held the vapour, and being transferred to a sensitive substance impressed a developable image. In like manner neutral bodies, such as mercury, alcohol, and ether, became active when very minute quantities of an active substance were added to them.

APPENDIX

LIST OF ELEMENTS

Names	Symbols	Atomic Weight
Aluminium	Al	27·3
Antimony	Sb	122
Arsenic	As	74·9
Barium	Ba	136·8
Bismuth	Bi	210
Boron	B	11
Bromine	Br	79·75
Cadmium	Cd	111·6
Cæsium	Cs	133
Calcium	Ca	39·9
Carbon	C	11·97
Cerium	Ce	141·2
Chlorine	Cl	35·37
Chromium	Cr	52·4
Cobalt	Co	58·6
Copper	Cu	63
Didymium	D	147
Erbium	E	169
Fluorine	F	19·1
Glucinium	Gl	9·3
Gold	Au	196·2
Hydrogen	H	1
Indium	In	113·4
Iodine	I	126·53
Iridium	Ir	196·7
Iron	Fe	55·9
Lanthanum	La	139
Lead	Pb	206·4
Lithium	Li	7·0
Magnesium	Mg	23·94
Manganese	Mn	54·
Mercury	Hg	199·8
Molybdenum	Mo	95·98
Nickel	Ni	58·16
Niobium	Nb	94
Nitrogen	N	14·01
Osmium	Os	198·6
Oxygen	O	15·96
Palladium	Pd	106·2

LIST OF ELEMENTS—*continued.*

Names	Symbols	Atomic Weight
Phosphorus	P	30·96
Platinum	Pt	196·7
Potassium	K	39·04
Rhodium	Rh	104·1
Rubidium	Rb	85·2
Ruthenium	Ru	103·5
Selenium	Se	78
Silicon	Si	28
Silver	Ag	107·66
Sodium	Na	22·99
Strontium	Sr	87·2
Sulphur	S	31·98
Tantalum	Ta	182
Tellurium	Te	128
Thallium	Tl	203·6
Thorium	Th	231·5
Tin	Sn	117·8
Titanium	Ti	48
Tungsten	W	184
Uranium	U	240
Vanadium	V	51·2
Yttrium	Y	93
Zinc	Zn	64·9
Zirconium	Zr	90

COMPARISON OF THE METRICAL WITH THE COMMON MEASURES

FROM DR. WARREN DE LA RUE'S TABLES

MEASURES OF LENGTH

	In English Inches	In English Feet = 12 Inches
Millimetre	0·03937	0·0032809
Centimetre	0·39371	0·0328090
Decimetre	3·93708	0·3280899
Metre	39·37079	3·2808992
Decametre	393·70790	32·8089920
Hectometre	3937·07900	328·0899200
Kilometre	39370·79000	3280·8992000
Myriometre	393707·90000	32808·9920000

1 Inch = 2·539954 Centimetres.
1 Foot = 3·0479449 Decimetres.

1 Yard = 0·91438348 Metre.
1 Mile = 1·6093149 Kilometre.

MEASURES OF SURFACE

	In English Square Feet	In English Sq. Yards =9 Square Feet
Centiare, or sq. metre	10·7642993	1·1960333
Are, or 100 sq. metres	1076·4299342	119·6033260
Hectare, or 10,000 sq. metres	107642·9934183	11960·3326020

1 Square Inch =6·4513669 Square Centimetres.
1 Square Foot =9·2899683 Square Decimetres.
1 Square Yard =0·83609715 Square Metre, or Centiare.
1 Acre =0·404671021 Hectare.

MEASURES OF CAPACITY

	In Cubic Inches	In Gallons=8 Pints =277·27384 Cubic Inches
Millilitre, or cubic centimetre	0·061027	0·00022010
Centilitre, or 10 cubic cents.	0·610271	0·00220097
Decilitre, or 100 cubic cents.	6·102705	0·02200967
Litre, or cubic decimetre	61·027052	0·22009668
Decalitre, or centistere	610·270515	2·20096677
Hectolitre, or decistere	6102·705152	22·00966767
Kilolitre, or stere, or cubic metre	61027·051519	220·09667675
Myriolitre, or decastere	610270·515194	2200·96676750

1 Cubic Inch =16·3861759 Cubic Centimetres.
1 Cubic Foot =28·3153119 Cubic Decimetres.
1 Gallon = 4·543457969 Litres.

MEASURES OF WEIGHT

	In English Grains	In Troy Ounces =480 Grains
Milligramme	0·015432	0·000032
Centigramme	0·154323	0·000322
Decigramme	1·543235	0·003215
Gramme	15·432349	0·032151
Decagramme	154·323488	0·321507
Hectogramme	1543·234880	3·215073
Kilogramme	15432·348800	32·150727
Myriogramme	154323·488000	321·507267

1 grain = 0·064798950 Gramme.
1 Troy oz. = 31·103496 Grammes.
1 lb. Avd. = 0·45359265 Kilogramme.
1 cwt. = 50·80237689 Kilogrammes.

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